KINETICS AND MECHANISM OF CATALYSED OXIDATION OF SOME ORGANIC COMPOUNDS

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CERTIFICATE

This is to certify that the work embodied in the thesis entitled " Kinetics and Mechanism of Catalysed oxidation of some organic compounds" has been carried out by Sri Kamlesh Kumar Dwivedi under my supervision. He has fulfilled the requirements for the degree of Doctor of Philosophy in Chemistry of Bundelkhand University, Jhansi, regarding the nature and prescribed period of investigational work. The work reported in this thesis embodies the work of the candidate himself.

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CHAPTER I

INTRODUCTION

1.1A : INTRODUCTION

Chemical kinetics is a part of science of motion. It is fundamentally concerned with the details of the process whereby a system gets converted from one state to another with the time required for transition. As in the case most of the branches of chemistry, reaction kinetics is an intimated blend of theory and experiment. However, "kinetics" of the reaction has been the main tool for arriving at conclusions. The subject of chemical kinetics is concerned with the detailed study of the rates of chemical reactions. The precise measurement of the rates of chemical processes and their variation with various parameters forms the experimental part of the subject. The interpretation of the results leads to an understanding of the complex reaction - mechanism. The elucidation of the reaction mechanisms, which proceeds almost exclusively through such experimental work, is usually supplemented by other evidences. Because of this, chemical kinetics is considered as an important branch of chemistry and has acquired enormous literature[1-9] in the recent past.

Oxidation of α - aminoacids by a variety of oxidants has been studied in detail by several investigators. As a class of oxidants, N - halogen compounds have received special attention[10-13] since these compounds act as sources of halogenium cations, hypohalite species and nitrogen anions which act both as bases and nucleophiles. The oxidative halogenation by N - halo compounds such as N - bromoacetamide (NBA), N - chloroacetamide (NCA) and N - bromosuccinimide (NBS)

offers a specific and rapid method for fragmenting high molecular weight peptides and proteins and this selective chemical method is the most useful method in peptide structure determination[14]. Hence the oxidative decarboxylation of α - aminoacids by N - halogeno compounds is an area of active experimentation. Therefore, in this chapter, the existing literature of the oxidation of α - aminoacids by various N - halogeno compounds is reviewed.

1.18 : REACTIONS WITH N-BROMOSUCCINIMIDE

The oxidation of α - aminoacids by NBS was reported by Schonberg *et al*[15] in 1951. At pH 4.7 and at temperature of about 30°C the oxidation of most of α - aminoacids proceeds smoothly. Carbon dioxide, ammonia and aldehydes related to the α - aminoacids so treated and containing one carbon atom less than the parent aminoacids, are the product usually produced from the aminoacids by the oxidation by NBS. At pH 4.7 and 30°C the decarboxylation of α - aminoacids by NBS resembles enzymic decarboxylation except for the fact that enzymic action leads to the production of the corresponding amine rather than ammonia and aldehyde.

A qualitative and quantitative study[16] was made on the gases evolved in the decarboxylation of aminoacids and their derivatives by NBS. The only gases evolved by treatment of aqueous solution of aminoacids with NBS at ambient temperatures were carbon dioxide and nitrogen[17]. In addition, the aldehydes

and nitriles corresponding to the decarboxylated aminoacids were formed. The formation of aldehyde was accompanied by the liberation of an equal amount of ammonia which was subsequently oxidised to nitrogen by NBS. The kinetics of oxidation of α - aminoacids by NBS were investigated only in early eighties even though the oxidation reactions themselves were reported quite earlier.

The kinetics of oxidation of α - aminoacids by NBS have been reported by Mushran <u>et al</u>.[18,19] and Bhargava <u>et al</u>[20] in acetic acid - water mixture. The two groups of workers have reported different mechanism and different oxidation products though the kinetics observed by them are similar. Bhargava proposed the abstraction of hydrogen from the neutral aminoacid by NBS in the rate determining step to give aldehyde as the final product.

$$R - \underset{NH_2}{\overset{H}{\overset{|}{\underset{|}{C}}}} - COOH \;+\; \underset{(NBS)}{>N - Br} \longrightarrow \underset{HOOC}{R - C} = NH + Br^- + \underset{(succinimide)}{>NH}$$

$$\xrightarrow{\text{Hydrolysis}} RCHO + NH_3 + CO_2$$

Mushran and Coworkers observed the formation of corresponding nitriles through the interaction of NBS with α - amino acid switter ion as follows :

$$RCH(\overset{+}{N}H_3)\;CO\overset{-}{O} + NBS \longrightarrow \underset{(Complex)}{Intermediate} \longrightarrow Product$$

The kinetics of oxidative decarboxylation of glycine, alanine and valine promoted by NBS have been studied extensively[21] as a function of pH and also in acid medium[22]. At pH 3.7 glycine obeys Michaelis Menten type of kinetic behaviour but shows substrate inhibition at pH 5.0. Both alanine and valine display zero order dependence on substrate concentration at pH 3.7, but exhibit Michaelis - Menten behaviour at pH 5.0. Solvent isotope effect and proton inventory technique were also studied. A mechanism involving the formation of acylhypobromite of glycine, which on slow decomposition gives an imine and subsequent rapid conversion of imine to products is proposed. Both alanine and valine undergo oxidation by a mechanism involving the slow abstraction of the hydrogen as hydride ion from the substrate as well as its acylhypobromite to give the imine.

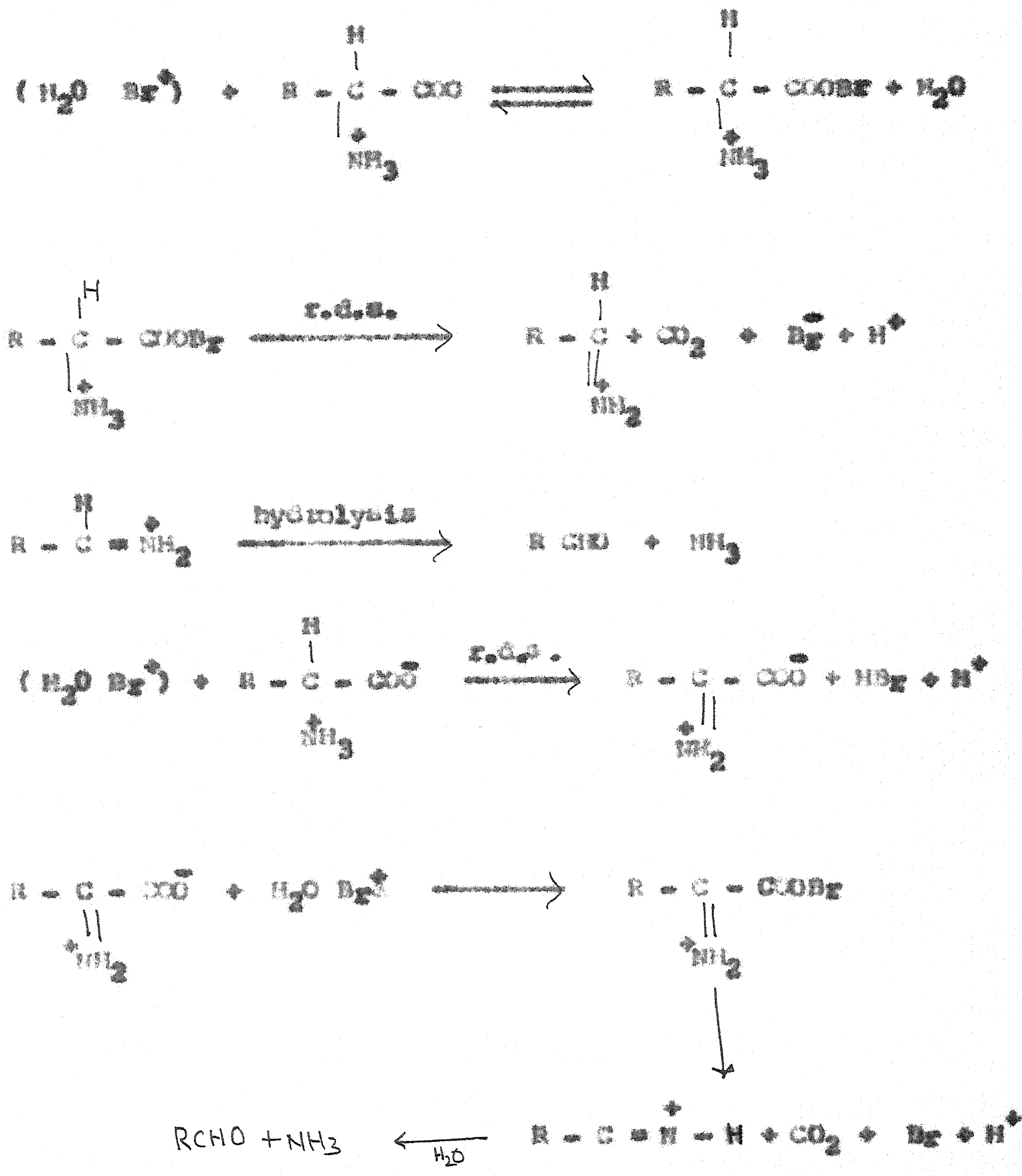
$$>N-Br \underset{H^+ \ (H_2O)}{\overset{\text{Hydrolysis}}{\rightleftharpoons}} (H_2O\,Br^+) + >NH$$

$$H_2O\,Br^+ + CH_2(\overset{+}{N}H_3)CO\bar{O} \xrightarrow[\text{r.d.s.}]{} CH_2(\overset{+}{N}H_3)COOBr + H_2O$$

$$CH_2(\overset{+}{N}H_3)COOBr \longrightarrow CH_2 = \overset{+}{N}H_2 + CO_2 + Br^- + H^+$$

$$\downarrow \text{Hydrolysis}$$

$$CH_2O + NH_3$$



The kinetics of oxidation of α - aminoacids by N-Chlorosuccinimide (NCS), the chlorine analogue of NBS, have been studied in aqueous alkaline medium[23] and in buffered medium[24] in the pH range 3.5 to 6.0. The observed

results show that in alkaline medium the mechanism could be written as :

$$>N-Cl + RCH(NH_2)COO^- \xrightarrow{\text{fast}} R-\overset{\displaystyle H}{\underset{\displaystyle H-N-H}{C}}-\overset{\displaystyle O}{\overset{\|}{C}}-O-Cl$$

(x)

$$x \longrightarrow \underbrace{R-CH=\overset{+}{N}H_2 + CO_2 + Cl^-} \xrightarrow{\text{hydrolysis}} RCHO + NH_3$$

In buffered medium, the mechanism differs from the one in alkaline medium in the respect that the first step is the equilibrium between α - aminoacyl hypochlorite and aminoacid switter ion as :

$$>N-Cl + R-CH(\overset{+}{N}H_3)\overset{-}{COO} \underset{H^+}{\rightleftharpoons} R-CH(\overset{+}{N}H_3)COOCl + >NH$$

(imide)

The α - amino acyl hypochlorite then decomposes in the rate determining step to give aldehyde and nitrile as the products. Formaldehyde catalyses the reaction at pH = 4.0 and this was explained[24] by the formation of Schiff's base between α - aminoacid and formaldehyde.

1.1C : REACTIONS WITH N-HALO p-TOLUENE SULPHONAMIDE

The earliest definite work on the oxidation of amino acid with N-chloro p-toluene sulphonamide was reported by Dakin[25] in 1916 - 1917. Dakin employed N-chloro p-toluene sulphonamide (generally known as chloramine - T or CAT) as the oxidising agent for a variety of aminoacids and reported that one mole of CAT per mole of aminoacid will cause the formation of aldehydes, carbondioxide and ammonia but two moles of this reagent will cause the production of nitriles.

The kinetics of oxidation of a number of aminoacids by chloramine-T in both acidic and alkaline media has been studied extensively[36-50]. Depending upon the pH of the medium CAT furnishes different types of reactive species in solution. N - chloro p-toluene sulphonamide (monochloramine-T, R N HCl, were R = pCH_3 ($C_6H_4SO_2$), dichloramine-T ($RNCl_2$), HOCl and possibly $H_2O\,Cl^+$ are the predominant species in acid solution and $RNCl^-$ and OCl^- ions are formed in alkaline medium. The oxidation process of α - aminoacids in acid media has been reported to proceed via, two paths, one involving the direct interaction of RNHCl with the neutral aminoacid in a slow step leading to the formation of N-chloro aminoacid which subsequently interacts with another molecule of RNHCl in a fast step to give N, N - dichloro aminoacid which in turn disproportionates to

yield the product nitrile and the other path involving the interection of Cl_2 or $H_2O\ Cl^+$, produced from the disproportionation of RNHCl in the presence or absence of Cl^- ion, with the substrate to give the product. In alkaline medium, the mechanism involving the interaction of R NHCl, HOCl, $RNCl^-$ and OCl^- with the substrate is proposed. The reaction scheme can be summarised as shown below : Acid Medium :

$$RNHCl + R'CH(NH_2)COOH \xrightarrow{r.d.s.} R'CH(NHCl)COOH\ (S')$$

$$S' + RNHCl \xrightarrow{Fast} Products$$

$$Cl_2 + R'CH(NH_2)COOH \xrightarrow{Fast} R'CH(NHCl)COOH\ (S')$$

$$S' + Cl_2 \xrightarrow{Fast} Products$$

$$H_2O\ Cl^+ + R'CH(NH_2)COOH \xrightarrow{Fast} R'CH(NHCl)COOH$$

$$S' + H_2O\ Cl^+ \xrightarrow{Fast} Products$$

Alkaline Medium :

$$RNHCl + R'CH(NH_2)COO^- \xrightarrow{r.d.s.} R'CH(NHCl)COO^-\ (S'')$$

$$S'' + R\ NHCl \xrightarrow{Fast} Products$$

$$R'CH(NH_2)COO^- + OCl^- \xrightarrow{r.d.s.} R'CH(NHCl)COO^-\ (S'')$$

$$S'' + OCl^- \xrightarrow{Fast} Products$$

$$R^{'}CH(NH_2)COO^- + OCl^- \xrightarrow{Fast} RCH(NHCl)COO^- \quad (S^*)$$

$$S^* + OCl^- \xrightarrow{Fast} Products$$

$$R^{'}CH(NH_2)COO^- + HOCl \xrightarrow{R.D.S.} R^{'}CH(NHCl)COO^- \quad (S^*)$$

$$S^* + HOCl \xrightarrow{Fast} Products.$$

The electrophilic attack of dichloramine-T ($RNCl_2$) at the carboxylate group of the aminoacid is also proposed[41,46] from the kinetic results in acidic medium. Kinetics of oxidation of α - aminoacids by N-bromo p-toluene sulphonamide[51-56] (BAT), N- Chloro benzene sulphonamide[57] (CAB) and N-bromobenzene sulphonamide[58,59] (BAB) were also extensively studied in both acidic and alkaline media. The kinetics and reaction mechanisms of the oxidants are similar to that of CAT.

1.2 : PRESENT WORK

It appears from the survey of literature that N-bromosuccinimide is a potent oxidant in acidic and alkaline media, but the literature on its oxidative capacity in the presence of homogeneous catalyst iridium (III) chloride in acidic or alkaline media is not known. Iridium (III) chloride although has been earlier attempted to obtain its catalytic potential in in N-bromoacetamide but in hydrochloric acid catalytic potential of iridium(III) chloride in redox system involving N-bromosuccinimide as oxidant and amino acids as reducing agents. Hence in the present work an attempt has been made to investigate the kinetics of iridium(III) chloride catalysed oxidation of glycine, alanine and valine by N-bromosuccinimide in hydrochloric acid using mercuric acetate as bromide ion scavenger. The kinetic data will be collected in the presence of potassium chloride. Since variation of ionic strength of the medium plays an important role in deciding the nature of reactive species of rate determining step, hence in the beginning it was attempted to see whether reactions were influenced by change in ionic strength of the medium. It was observed that ionic strength did not influence the rate of the reaction. Hence all reactions were studied without maintaining ionic strength of the medium constant.

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CHAPTER II

MATERIALS AND METHOD OF INVESTIGATION

2.1 : CHEMICALS USED AND PREPARATION OF THEIR SOLUTIONS

(A) The solutions of glycine, alanine and valine (Loba chemie) were prepared by dissolving their desired and weighed samples in doubly distilled water. Amino acids used here were samples of highest purity available and hence they were used as such.

(B) The solution of N-bromosuccinimide (E.Merck) was prepared by dissolving its weighed recrystallised sample in doubly distilled water. Its solution was standardised by estimating its active bromine by iodometric estimations.

(C) The solution of iridium (III) chloride (Johnson and Matthey) was prepared from its 1 gm sample by dissolving it in 200 ml of 0.1N HCl and then it was diluted to one litre for stock solution. Its strength was calculated and strength of HCl was also calculated in the stock solution.

(D) Solution of mercuric acetate (E.Merck) was prepared by dissolving its weighed sample in tripled distilled water containing 5% acetic acid.

(E) Hydrochloric acid solution prepared was standardised with standard solution of sodium hydroxide which itself was standardised by standard solution of oxalic acid (BDH).

(f) Solution of sodium thiosulphate (also known as hypo) was prepared by dissolving the weighed amount of its sample (E.Merck) in doubly distilled water. The prepared solution was further standardised with standard solution of copper sulphate iodometrically.

(g) The solution of potassium chloride (BDH) was prepared by directly weighed sample in distilled water.

(h) Solution of succinimide was prepared by dissolving its weighed sample (E. Merck) in doubly distilled water.

(i) Solution of sodium perchlorate was prepared by dissolving its E. Merck (Germany) sample in desired quantity in known volume of distilled water.

(j) 10% solution of potassium iodide was freshly prepared each day.

(k) 1% starch solution was prepared.

2.2 : METHOD OF INVESTIGATION

The kinetic investigations were carried out by following the procedure given here. Requisite volume of standard solution of reducing amino acids used here, hydrochloric acid, mercuric acetate, iridium (III) chloride, potassium chloride and other reagents, if any, were taken in a reaction vessel which was kept in an electrically operated thermostatic water bath set at desired temperature. The required volume of N-bromo-succinimide standard solution was also taken in another vessel which was also placed in the same thermostat for thermal equilibrium. When solutions of both the vessels had attained the desired temperature, the solutions of both the vessels were mixed vigorously and the stop watch was started at the time of mixing. An aliquot of reaction mixture was taken out and time was noted as zero time and this portion of reaction mixture was estimated for NBS iodometrically. The progress of the reaction was monitored by determining the remaining NBS at different times of intervals.

The velocity constant of the reaction was calculated with the help of readings noted at different time of intervals. A plot of $(a - x)$ against 'time' was plotted for different concentrations of NBS (where 'a-x' is the

concentrations of NBS at different times). When the reaction has proceeded hardly 10% a tangent at point on the curve is drawn. The point corresponds to 10 minutes. The slope of the tangent gave the value[1] of ($\frac{-dc}{dt}$). The concentration at which ($\frac{-dc}{dt}$) is determined has been designated as $[NBS]^*$. The order of the reaction with respect to NBS is calculated with the help of ($\frac{-dc}{dt}$) values obtained at different concentrations of NBS. Now when the order of the reaction with respect to NBS is determined and ascertained, the velocity constant of the determined order with respect to NBS is divided by the concentration of other reactant with respect to which order of the reaction is to be determined. This way the order of the reaction with respect to each reactant is ascertained.

2.3 : STOICHIOMETRY AND PRODUCT ANALYSIS

Various sets of experiments were carried out with different [NBS] : [Amino acid] ratios. Estimation of remaining NBS showed that one mole of NBS was consumed to oxidise one mole of each of amino acids used here and accordingly following stoichiometric eqn (1) is formulated where R stands for $-H$, $-CH_3$ and $(CH_3)_2CH-$ in glycine, alanine and valine respectively.

$$\left.\begin{array}{l} CH_2CO \\ | \\ CH_2CO \end{array}\right\rangle NBr + RCH(NH_2)COOH \xrightarrow{H_2O}$$

$$RCHO + NH_3 + CO_2 + \left.\begin{array}{l} CH_2\ CO \\ | \\ CH_2\ CO \end{array}\right\rangle NH_2 \qquad \ldots\ldots \quad (1)$$

The corresponding aldehydes were identified as end products in oxidation of each amino acids.

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CHAPTER III

COMPUTATION OF ORDER OF REACTION WITH RESPECT TO OXIDANT IN NBS–AMINO ACIDS REDOX SYSTEMS WITH Ir(III) AS CATALYST

3 : COMPUTATION OF ORDER OF THE REACTION IN N-BROMOSUCCINIMIDE IN Ir(III) CATALYSED OXIDATION OF SOME AMINO ACIDS IN ACIDIC MEDIA

This chapter includes the study of kinetics of oxidation of iridium (III) chloride catalysed oxidation of some amino acids such as glycine, alanine and valine by N - bromosuccinimide in the presence of hydrochloric acid. Preliminary investigations indicated that with the progress of the reaction a pale yellow colour developed in the reaction mixture after 10 - 15% of the reaction has proceeded. As a result of this development it was also observed that reaction which was proceeding slowing, became faster. This was ascribed to appearance of Br_2 in the reaction as a result of interaction between N-bromosuccinimide and Br^- (produced in the reaction). This produced bromine sets parallel oxidation process and thus complicates the study of the title reaction. Preliminary studies also showed negligible effect of variation of ionic strength of the medium on the reaction rate. Hence all reactions have been carried out without keeping ionic strength of the medium constant.

In order to solve the problem of parallel oxidation of amino acids by Br_2 experiment was carried out in the presence of mercuric acetate which acted as Br^- scavenger in the reaction mixture. It was observed that appearance

of yellow colour was stopped. Hence all experiments were carried out in the presence of mercuric acetate whose presence in the reaction pure N-bromosuccinimide oxidation of amino acids without any complications.

In order to determine the order of the reaction with respect to N-bromosuccinimide (NBS), several experiments containing different concentrations of NBS and at fixed concentrations of all other reactants under isolation conditions have been carried out. In each experiments concentration of NBS was always lower than that of amino acid at least five times. The results of various experiments have been recorded in tables 3.1 - 3.8, 3.9 - 3.16 and 3.17 - 3.24 in oxidation of glycine, alanine and valine respectively. The value of zero - order rate constant i.e. ($\frac{-dc}{dt}$) in each table has been determined from the slope of the curve drawn between remaining NBS and time. The slope is determined at fixed time when hardly 10 - 15% reaction has proceeded. The value of [NBS] at which ($^{-dc}/_{dt}$) has been determined is designated as $[NBS]^{*}$ in each table. Iridium (III) chloride has been written as Ir(III) in each table.

TABLE 3.1

[NBS] = 4.00×10^{-4} M, [Glycine] = 2.00×10^{-2} M

[HCl] = 4.00×10^{-2} M, [Ir(III)] = 4.80×10^{-6} M

[KCl] = 1.00×10^{-2} M, [Hg(OAc)$_2$] = 3.34×10^{-3} M

Temperature 30°C

Time (min.)	ml of hypo (M/1800)	[NBS]* $\times 10^{4}$ M	$\left(-\frac{dc}{dt}\right) \times 10^{7}$ M L^{-1} s^{-1}
00	7.20		
05	5.76		
10	4.72		
15	4.06		
20	3.66	3.15	1.21
25	3.12		
30	2.76		
35	2.70		
40	2.32		

TABLE 3.2

[NBS] = 5.00×10^{-4} M, [Glycine] = 2.00×10^{-2} M

[HCl] = 4.00×10^{-2} M, [Ir(III)] = 4.80×10^{-6} M

[KCl] = 1.00×10^{-2} M, [Hg(OAc)$_2$] = 3.34×10^{-3} M

Temperature 30°C

Time (min.)	ml of hypo (N/1800)	[NBS]* $\times 10^4$ M	$(-dc/dt) \times 10^7$ M L^{-1} s^{-1}
00	9.00		
05	8.22		
10	7.66		
20	6.38		
30	5.48	4.60	1.38
50	3.50		
60	3.02		
70	2.76		

TABLE 3.3

[NBS] = 6.67x10^{-4}M, [Glycine] = 2.00x10^{-2}M

[HCl] = 4.00x10^{-2}M, [Ir(III)] = 4.80x10^{-6}M

[KCl] = 1.00x10^{-2}M, [Hg(OAc)$_2$] = 3.34x10^{-3}M

Temperature 30°C

Time (min.)	ml of hypo (N/1800)	[NBS]* x 10^{4}M	($\frac{-dc}{dt}$) x 10^7 M L^{-1} s^{-1}
00	12.02		
05	10.70		
10	8.98		
20	8.30		
30	7.04	6.20	1.61
40	5.96		
50	5.12		
60	4.40		
70	3.86		

TABLE 3.4

[NBS] = 8.00 x 10^{-4} M, [Glycine] = 2.00x10^{-2} M

[HCl] = 4.00x10^{-2} M, [Ir(III)] = 4.80x10^{-6} M

[KCl] = 1.00x10^{-2} M, [Hg(OAc)$_2$] = 3.34x10^{-3} M

Temperature 30°C

Time (min.)	ml of hypo (M/882)	[NBS]* x 10^4 M	($\frac{-dc}{dt}$) x 10^7 M L^{-1} s^{-1}
00	7.06		
05	6.50		
10	6.14		
20	5.42		
30	4.74		
40	4.10	7.45	2.08
60	3.48		
80	3.12		
100	2.84		

TABLE 3.5

$[NBS] = 13.33\times10^{-4}M$, $[Glycine] = 2.00\times10^{-2}M$

$[HCl] = 4.00\times10^{-2}M$, $[Ir(III)] = 4.80\times10^{-6}M$

$[KCl] = 1.00\times10^{-2}M$, $[Hg(OAc)_2] = 3.34\times10^{-3}M$

Temperature $30^{\circ}C$

Time (min.)	ml of hypo (M/882)	$[NBS]^{*} \times 10^{4}M$	$\left(\frac{-dc}{dt}\right) \times 10^{7}$ $M\ L^{-1}\ s^{-1}$
00	11.72		
05	10.82		
10	10.04		
20	8.76		
40	7.02	12.30	3.34
60	6.18		
90	5.40		
130	4.74		
170	4.62		

TABLE 3.6

[NBS] = 16.67x10^{-4}M, [Glycine] = 2.00x10^{-2}M

[HCl] = 4.00x10^{-2}M, [I_r(III)] = 4.80x10^{-6}M

[KCl] = 1.00x10^{-2}M, [Hg(OAc)$_2$] = 3.34x10^{-3}M

Temperature 30°C

Time (min.)	ml of hypo (M/490)	[NBS]* x 10^4M	($\frac{-dc}{dt}$)x10^7 M L^{-1} s^{-1}
00	8.12		
05	7.02		
10	5.98		
20	4.94		
30	4.44	15.20	4.00
50	2.98		
70	2.36		
90	2.16		
110	1.98		

TABLE 3.7

$[NBS] = 20.00 \times 10^{-4}$ M, $[Glycine] = 2.00 \times 10^{-2}$ M

$[HCl] = 4.00 \times 10^{-2}$ M, $[I_r(III)] = 4.80 \times 10^{-6}$ M

$[KCl] = 1.00 \times 10^{-2}$ M, $[Hg(OAc)_2] = 3.34 \times 10^{-3}$ M

Temperature $30^{\circ}C$

Time (min.)	ml of hypo (N/490)	$[NBS]^{*} \times 10^{4}$ M	$\left(\frac{-dc}{dt}\right) \times 10^{7}$ M L^{-1} s^{-1}
00	9.76		
05	8.62		
10	7.94		
20	6.84		
30	5.86	18.40	4.62
40	5.04		
60	3.86		
80	3.10		
100	2.52		

TABLE 3.8

[NBS] = 25.00×10^{-4}M, [Glycine] = 2.00×10^{-2}M

[HCl] = 4.00×10^{-2}M, [Ir(III)] = 4.80×10^{-6}M

[KCl] = 1.00×10^{-2}M, [$Hg(OAc)_2$] = 3.34×10^{-3}M

Temperature 30°C

Time (min.)	ml of hypo (M/490)	[NBS]* x 10^4M	$\left(\frac{-dc}{dt}\right)\times10^7$ M L^{-1} s^{-1}
00	12.20		
05	10.76		
10	9.78		
20	8.42		
30	7.20	22.90	5.02
40	6.04		
50	5.48		
60	4.80		
80	4.20		

TABLE 3.9

[NBS] = 4.00x10^{-4}M, [Alanine] = 2.00x10^{-2}M

[HCl] = 10.00x10^{-2}M, [Ir(III)] = 4.80x10^{-6}M

[KCl] = 1.00x10^{-2}M, [Hg(OAc)$_2$] = 3.34x10^{-3}M

Temperature 30°C

Time (min.)	ml of hypo (N/1802)	[NBS]* x10^4	($\frac{-dc}{dt}$)x10^7 M L^{-1} s^{-1}
00	7.20		
05	6.66		
10	6.40		
20	5.82	3.75	0.70
30	5.20		
40	4.78		
60	3.68		
80	3.02		
100	2.56		

TABLE 3.10

$[NBS] = 5.00\times10^{-4}$ M, $[Alanine] = 2.00\times10^{-2}$ M

$[HCl] = 10.00\times10^{-2}$ M, $[Ir(III)] = 4.80\times10^{-6}$ M

$[KCl] = 1.00\times10^{-2}$ M, $[Hg(OAc)_2] = 3.34\times10^{-3}$ M

Temperature $30^{o}C$

Time (min.)	ml of hypo (N/1802)	$[NBS]^{*} \times10^{4}$ M	$\left(\frac{-dc}{dt}\right)\times10^{7}$ $M\ L^{-1}\ s^{-1}$
00	9.00		
05	8.54		
10	8.14		
20	7.52		
30	7.02	4.75	0.84
50	5.32		
70	4.32		
90	3.50		
110	3.12		

TABLE 3.11

[NBS] = 6.67x10^{-4}M, [Alanine] = 2.00x10^{-2}M

[HCl] = 10.00x10^{-2}M, [Ir(III)] = 4.80x10^{-6}M

[KCl] = 1.00x10^{-2}M, [Hg(OAc)$_2$] = 3.34x10^{-3}M

Temperature 30°C

Time (min.)	ml of hypo (N/1802)	[NBS]* x 10^{4}M	($\frac{-dc}{dt}$)x10^{7} M L^{-1} s^{-1}
00	11.98		
05	11.54		
10	10.74		
20	10.18		
30	8.24		
50	6.92	6.30	
70	5.58		
90	4.72		
110	3.92		

TABLE 3.12

$[NBS] = 8.00 \times 10^{-4}M$, $[Alanine] = 2.00 \times 10^{-2}M$

$[HCl] = 10.00 \times 10^{-2}M$, $[Ir(III)] = 4.80 \times 10^{-6}M$

$[KCl] = 1.00 \times 10^{-2}M$, $[Hg(OAc)_2] = 3.34 \times 10^{-3}M$

Temperature $30^{\circ}C$

Time (min.)	ml of hypo (N/890)	$[NBS]^{*} \times 10^{4}M$	$(\frac{-dc}{dt}) \times 10^{7}$ $M\,l^{-1}\,s^{-1}$
00	7.06		
05	6.48		
10	6.32		
20	5.88		
40	4.64	7.60	1.38
60	4.28		
90	3.68		
120	3.32		
160	2.98		

TABLE 3.13

$[NBS] = 13.33 \times 10^{-4} M$, $[Alanine] = 2.00 \times 10^{-2} M$

$[HCl] = 10.00 \times 10^{-2} M$, $[I_r(III)] = 4.80 \times 10^{-6} M$

$[Hg(OAc)_2] = 3.34 \times 10^{-3} M$, $[KCl] = 1.00 \times 10^{-2} M$

Temperature $30^{\circ}C$

Time (min.)	mls of hypo (M/890)	$[NBS]^* \times 10^4 M$	$(\frac{-dc}{dt}) \times 10^7$ $M\ l^{-1}\ s^{-1}$
00	11.72		
05	10.98		
10	10.50		
20	9.64		
40	8.60		
70	6.82	12.60	2.00
110	5.74		
150	5.08		
200	4.96		

TABLE 3.14

[NBS] = 16.67×10^{-4}M, [Alanine] = 2.00×10^{-2}M

[HCl] = 10.00×10^{-2}M, [I_r(III)] = 4.80×10^{-6}M

[KCl] = 1.00×10^{-2}M, [Hg(OAc)$_2$] = 3.34×10^{-3}M

Temperature 30°C

Time (min.)	ml of hypo (N/430)	[NBS]* $\times10^4$M	$\left(\frac{-dc}{dt}\right)\times10^7$ M L^{-1} s^{-1}
00	7.12		
05	6.86		
10	6.72		
20	6.22		
40	5.52		
70	4.76	16.00	2.16
90	4.28		
120	3.94		
180	3.36		

TABLE 3.15

[NBS] = 20.00x10^{-4}M, [Alanine] = 2.00x10^{-2}M

[HCl] = 10.00x10^{-2}M, [Ir(III)] = 4.80x10^{-6}M

[KCl] = 1.00x10^{-2}M, [Hg(OAc)$_2$] = 3.34x10^{-3}M

Temperature 30^{o}C

Time (min.)	ml of hypo (N/430)	[NBS]* x10^4M	($\frac{-dc}{dt}$)x10^7 M L^{-1} s^{-1}
00	8.56		
05	8.14		
10	7.84		
20	7.18		
40	6.54	19.00	2.60
70	5.24		
100	4.62		
140	4.14		
200	3.48		

TABLE 3.16

$[NBS] = 25.00 \times 10^{-4} M$, $[Alanine] = 2.00 \times 10^{-2} M$

$[HCl] = 10.00 \times 10^{-2} M$, $[Ir(III)] = 4.80 \times 10^{-6} M$

$[KCl] = 1.00 \times 10^{-2} M$, $[Hg(OAc)_2] = 3.34 \times 10^{-2} M$

Temperature 30°C

Time (mins.)	ml of hypo (M/430)	$[NBS]^* \times 10^4 M$	$\left(\frac{-dc}{dt}\right) \times 10^7$ $M\ L^{-1}\ s^{-1}$
00	10.70		
05	10.26		
10	9.94		
20	9.26		
40	8.46	24.00	2.60
70	6.96		
100	6.06		
140	5.34		
200	4.80		

TABLE 3.17

$[NBS] = 4.00 \times 10^{-4} M$, $[Valine] = 2.00 \times 10^{-2} M$

$[HCl] = 4.00 \times 10^{-2} M$, $[I_r(III)] = 4.80 \times 10^{-6} M$

$[KCl] = 1.00 \times 10^{-2} M$, $[Hg(OAc)_2] = 3.34 \times 10^{-3} M$

Temperature 30°C

Time (min.)	ml of hypo (M/1060)	$[NBS]^* \times 10^4$ M	$\left(\frac{-dc}{dt}\right) \times 10^7$ M L^{-1} s^{-1}
00	7.44		
05	7.12		
10	6.96		
20	6.62		
40	5.50	3.90	0.53
60	4.74		
80	3.78		
100	3.10		
120	2.34		

TABLE 3.18

$[NBS] = 5.00\times10^{-4}$ M, $[Valine] = 2.00\times10^{-2}$ M

$[HCl] = 4.00\times10^{-2}$ M, $[Ir(III)] = 4.80\times10^{-6}$ M

$[KCl] = 1.00\times10^{-2}$ M $[Hg(OAc)_2] = 3.34\times10^{-2}$ M

Temperature $30^{\circ}C$

Time (min.)	ml of hypo (M/1860)	$[NBS]^* \times 10^4$ M	$\left(\frac{-dc}{dt}\right) \times 10^7$ M L^{-1} s^{-1}
00	9.32		
05	8.98		
10	8.70		
20	7.86		
40	6.48	4.80	0.64
60	5.42		
80	4.34		
100	3.36		
120	2.72		

TABLE 3.19

[NBS] = 6.67×10^{-4} M, [Valine] = 2.00×10^{-2} M

[HCl] = 4.00×10^{-2} M, [Ir(III)] = 4.80×10^{-6} M

[KCl] = 1.00×10^{-2} M, [Hg(OAc)$_2$] = 3.34×10^{-3} M

Temperature 30°C

Time (min.)	ml of hypo (N/1860)	$[NBS]^* \times 10^4$ M	$(\frac{-dc}{dt}) \times 10^7$ M L^{-1} s^{-1}
00	12.44		
05	12.12		
10	11.92		
20	10.62		
40	9.30	6.40	0.84
60	7.42		
80	4.52		
100	4.52		
120	3.52		

TABLE 3.20

[NBS] = 8.00×10^{-4} M, [Valine] = 2.00×10^{-2} M

[HCl] = 4.00×10^{-2} M, [Ir(III)] = 4.80×10^{-6} M

[KCl] = 1.00×10^{-2} M, [Hg(OAc)$_2$] = 3.34×10^{-3} M

Temperature 30^{o}C

Time (min.)	ml of hypo (N/948)	[NBS]* $\times 10^{4}$ M	$\left(\frac{-dc}{dt}\right) \times 10^{7}$ M L^{-1} s^{-1}
00	7.58		
05	7.42		
10	7.16		
20	6.76		
40	5.82		
60	4.82	7.70	1.00
90	4.08		
120	3.08		
160	2.32		
200	1.92		

TABLE 3.21

[NBS] = 13.33x10^{-4}M, [Valine] = 2.00x10^{-2}M

[HCl] = 4.00x10^{-2}M, [Ir(III)] = 4.80x10^{-6}M

[KCl] = 1.00x10^{-2}M, [Hg(OAc)$_2$] = 3.36x10^{-3}M

Temperature 30^{o}C

Time (min.)	ml of hypo (N/948)	[NBS]* x 10^{4}M	$(\frac{-dc}{dt})$ x 10^{7} M L^{-1} S^{-1}
00	12.64		
05	12.44		
10	12.08		
20	11.42		
40	10.26	13.00	1.66
80	7.86		
140	5.44		
200	4.34		
260	1.98		

TABLE 3.22

[NBS] = 16.67×10^{-4} M, [Valine] = 2.00×10^{-2} M

[HCl] = 4.00×10^{-2} M, [Ir(III)] = 4.80×10^{-6} M

[KCl] = 1.00×10^{-2} M, [Hg(OAc)$_2$] = 3.34×10^{-3} M

Temperature 30°C

Time (min.)	ml of hypo (N/460)	$[NBS]^* \times 10^4$ M	$(\frac{-dc}{dt}) \times 10^7$ M L^{-1} S^{-1}
00	7.66		
05	7.50		
10	7.32		
20	6.72		
40	5.82	16.20	1.78
60	5.02		
120	3.12		
180	2.34		
240	1.92		

TABLE 3.23

$[NBS] = 20.00 \times 10^{-4} M$, $[Valine] = 2.00 \times 10^{-2} M$

$[HCl] = 4.00 \times 10^{-2} M$, $[Ir(III)] = 4.80 \times 10^{-6} M$

$[KCl] = 1.00 \times 10^{-2} M$, $[Hg(OAc)_2] = 3.34 \times 10^{-3} M$

Temperature $30^{\circ}C$

Time (min.)	ml of hypo (M/460)	$[NBS]^{*} \times 10^{4} M$	$\left(\frac{-dc}{dt}\right) \times 10^{7}$ $M\ L^{-1}\ s^{-1}$
00	9.20		
05	8.92		
10	8.50		
20	7.82		
40	6.68	19.20	2.20
70	5.48		
130	3.76		
190	3.02		
250	2.36		

TABLE 3.24

[NBS] = 25.00×10^{-4} M, [Valine] = 2.00×10^{-2} M

[HCl] = 4.00×10^{-2} M, [Ir(III)] = 4.80×10^{-6} M

[KCl] = 1.00×10^{-2} M, $[Hg(OAc)_2]$ = 8.88×10^{-3} M

Temperature $30^{\circ}C$

Time (min.)	ml of hypo (M/460)	$[NBS]' \times 10^{4}$ M	$\left(\frac{-dc}{dt}\right) \times 10^{7}$ M l^{-1} s^{-1}
00	11.50		
05	11.20		
10	10.86		
20	10.24		
40	9.16	24.30	2.30
80	6.84		
140	4.80		
200	3.80		
260	1.08		

The kinetic results recorded in tables 3.1 - 3.8, 3.9 - 3.16 and 3.17 - 3.24 have been summarised in tables 3.25, 3.26 and 3.27 respectively.

TABLE 3.25

[Glycine] = 2.00×10^{-2} M, [HCl] = 4.00×10^{-2} M

[Ir(III)] = 4.80×10^{-6} M, [KCl] = 1.00×10^{-2} M

[Hg(OAc)$_2$] = 3.34×10^{-3} M, Temperature 30°C

[NBS] $\times 10^4$ M	[NBS]* $\times 10^4$ M	$(-dc/dt) \times 10^7$ M L^{-1} s^{-1}
4.00	3.15	1.21
5.00	4.60	1.38
6.67	6.20	1.61
8.00	7.45	2.08
13.33	12.30	3.34
16.67	15.20	4.00
20.00	18.40	4.42
25.00	22.90	5.02

TABLE 3.26

[Alanine] = 2.00×10^{-2} M, [HCl] = 10.00×10^{-2} M

[I_r(III)] = 4.80×10^{-6} M, [KCl] = 1.00×10^{-2} M

[Hg(OAc)$_2$] = 3.34×10^{-3} M, Temperature 30°C

[NBS] $\times 10^4$ M	[NBS]* $\times 10^4$ M	$\left(\frac{-dc}{dt}\right) \times 10^7$ M L^{-1} s^{-1}
4.00	3.75	0.70
5.00	4.75	0.84
6.67	6.30	1.10
8.00	7.60	1.38
13.33	12.60	2.00
16.67	16.00	2.16
20.00	19.00	2.60
25.00	24.00	2.60

TABLE 3.27

[Valine] = 2.00×10^{-2} M, [HCl] = 4.00×10^{-2} M

[KCl] = 1.00×10^{-2} M, [Ir(III)] = 4.80×10^{-6} M

[Hg(OAc)$_2$] = 3.34×10^{-3} M, Temperature 30°C

[NBS] $\times 10^{4}$ M	[NBS]* $\times 10^{4}$ M	$\left(\frac{-dc}{dt}\right) \times 10^{7}$ M L^{-1} s^{-1}
4.00	3.90	0.53
5.00	4.80	0.64
6.67	6.40	0.84
8.00	7.70	1.00
13.33	13.00	1.66
16.67	16.20	1.78
20.00	19.20	2.20
25.00	24.30	2.30

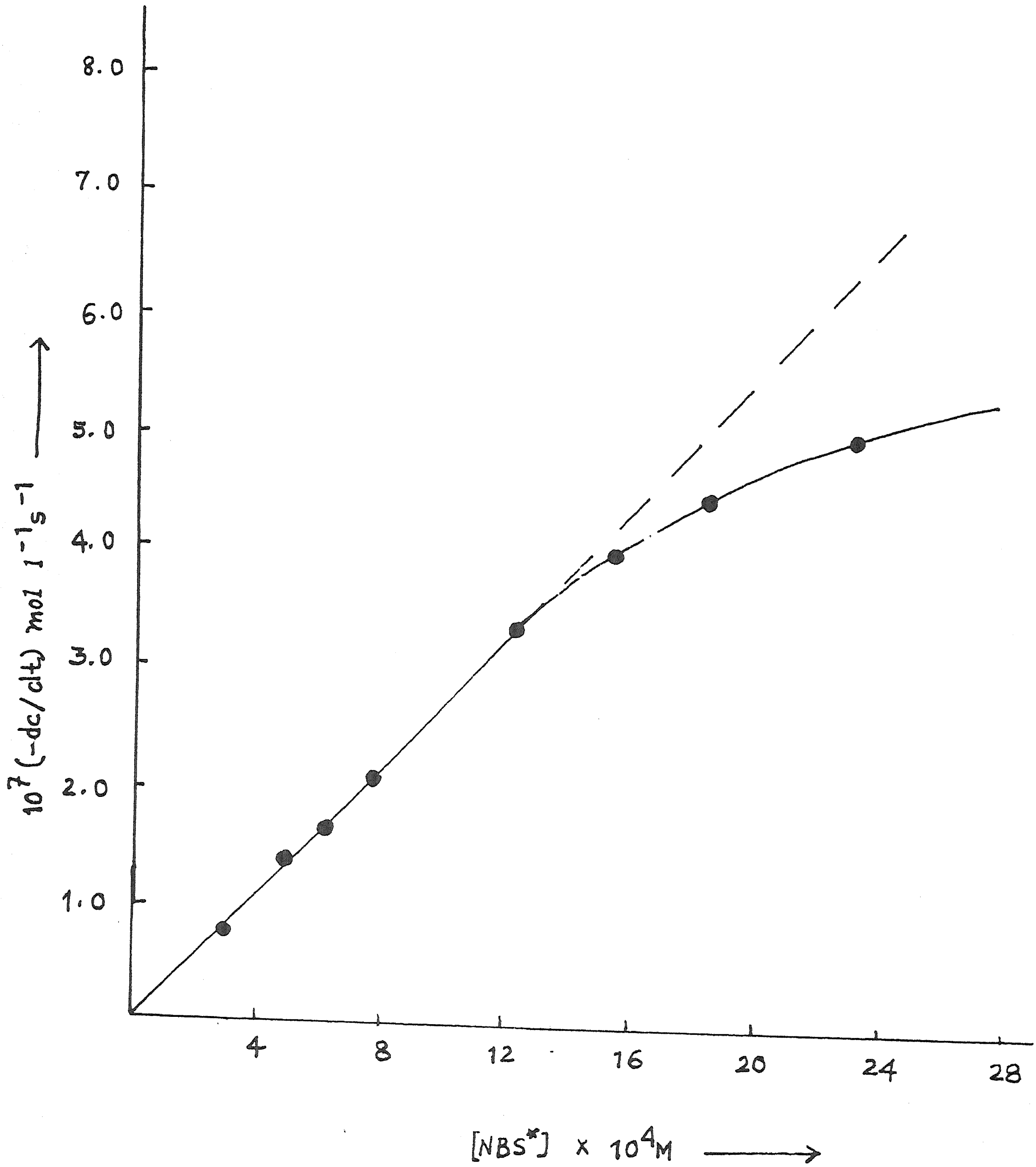

Fig. 3.1 Plot between (-dc/dt) and [NBS*]

[Glycine] = 2.00×10^{-2}M, [Ir(III)] = 4.80×10^{-6}M

[HCl] = 4.00×10^{-2}M, [KCl] = 1.00×10^{-2}M

[$Hg(OAc)_2$] = 3.34×10^{-3}M Temperature 30°C

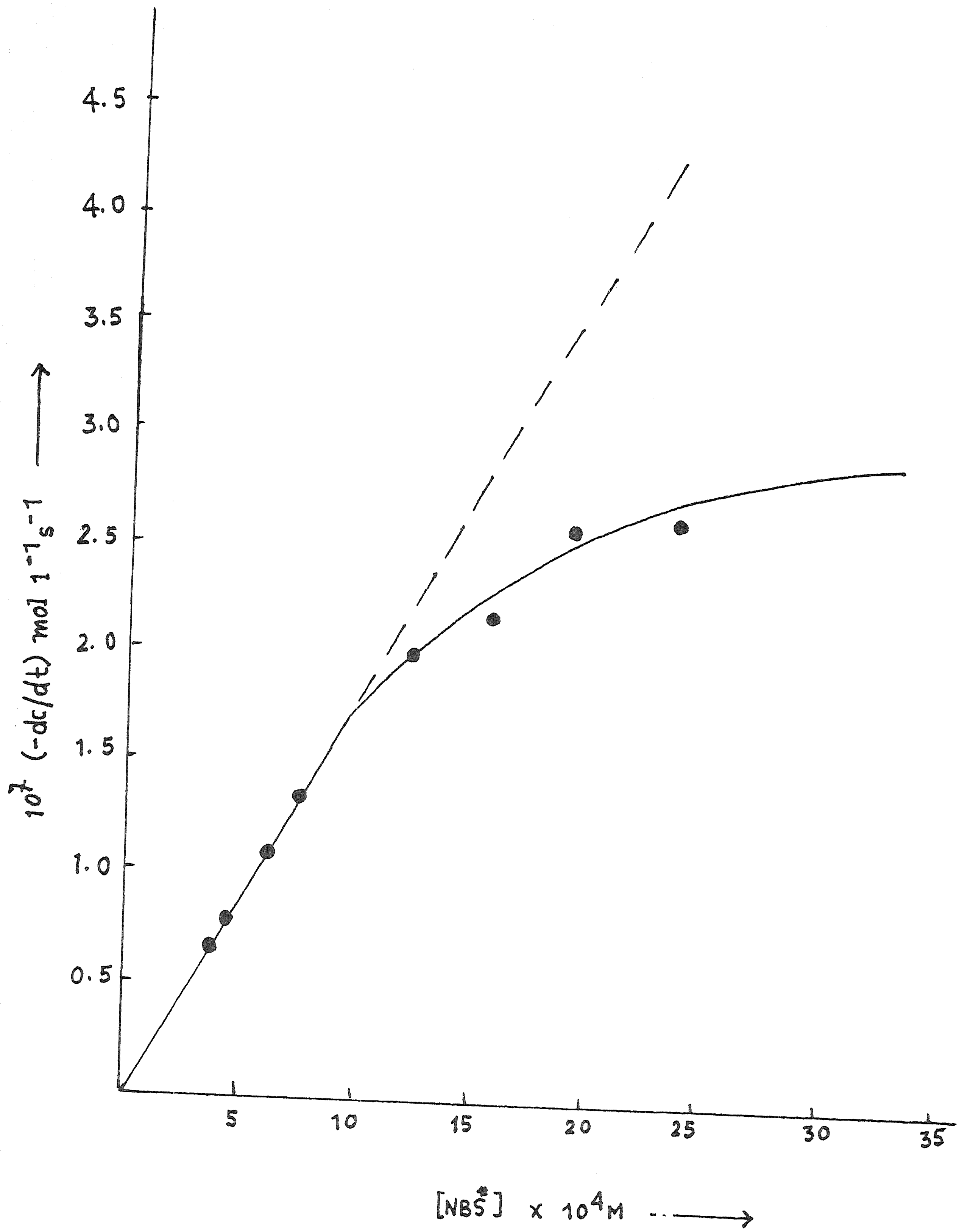

Fig. 3.2 : Plot between (-dc/dt) and [NBS*]

[Alanine] $= 2.00 \times 10^{-2}$M, $[Hg(OAc)_2] = 3.34 \times 10^{-3}$M

[HCl] $= 10.00 \times 10^{-2}$M, [Ir(III)] $= 4.80 \times 10^{-6}$M

[KCl] $= 1.00 \times 10^{-2}$M and Temperature 30°C

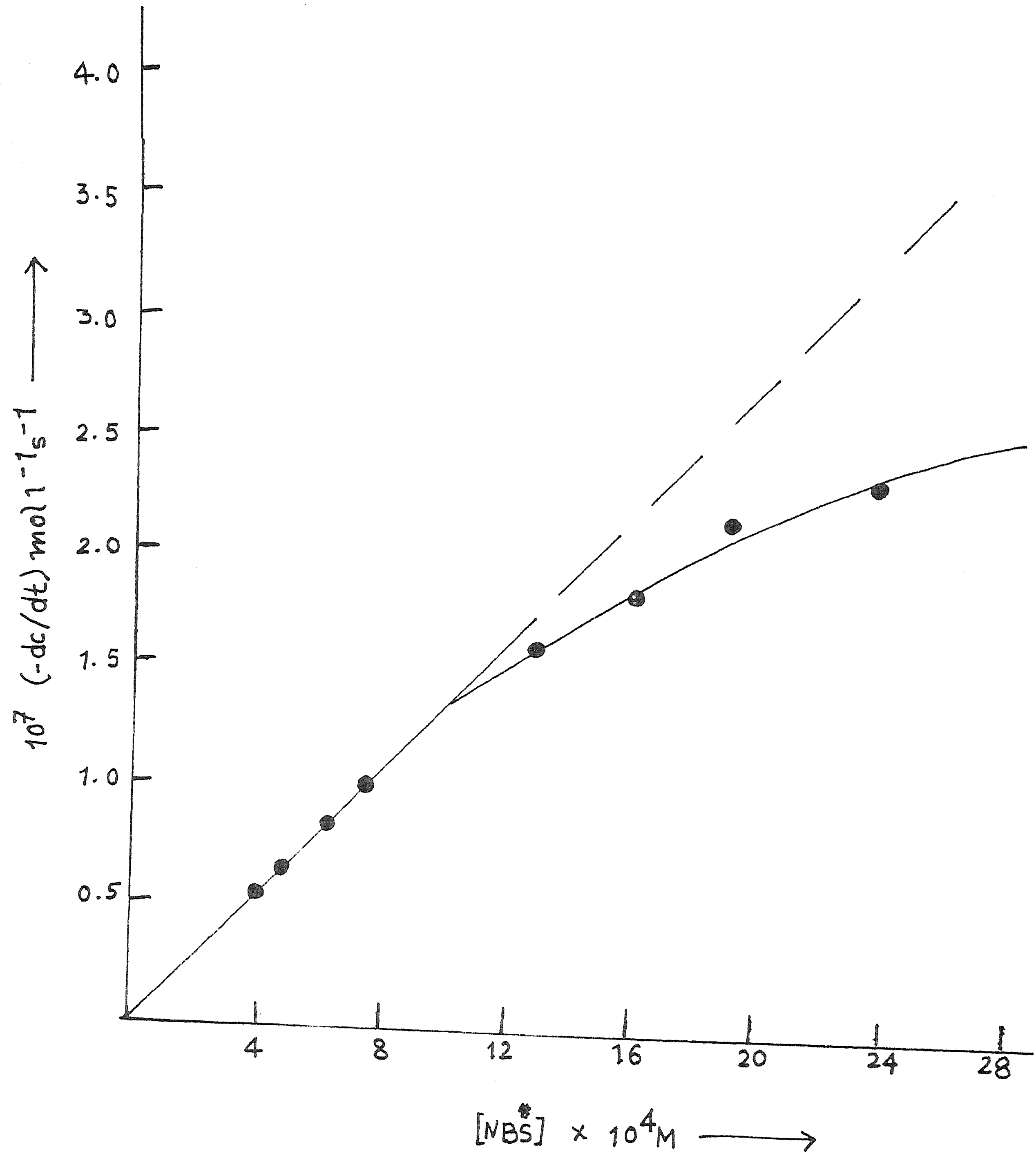

Fig. 3.3 : Plot between (-dc/dt) and [NBS*]

[Valine] = 2.00×10^{-2}M , [$Hg(OAc)_2$] = 3.34×10^{-3}M

[HCl] = 4.00×10^{-2}M , [Ir(III)] = 4.80×10^{-6}M

[KCl] = 1.00×10^{-2}M and Temperature 30°C

It is quite clear from the kinetic results of tables 3.25, 3.26 and 3.27 that in lower concentration range of NBS the value of ($-dc/dt$) increases linearly but at higher concentrations of NBS the value of ($-dc/dt$) tends to attain constant values. This indicates that oxidation of glycine, alanine and valine follows first - order kinetics in NBS at its lower concentration range but first - order kinetics in NBS tends to zero order at its higher concentration range.

The above observation is further supported by graphs plotted between ($\frac{-dc}{dt}$) and $[NBS]^*$. The curves are linear in lower concentration range of NBS while curve tends to attain the limiting value in higher concentration range of NBS (Fig. 3.1, 3.2 and 3.3). Hence it can be concluded that oxidation of glycine, alanine and valine follows first - order kinetics in NBS at low [NBS] and first - order dependence on NBS tends to zero - order at high concentration range of NBS.

CHAPTER IV

COMPUTATION OF ORDER OF REACTION WITH RESPECT TO REDUCING AMINO ACIDS IN REDOX SYSTEMS WITH Ir(III) AS CATALYST

4 : COMPUTATION OF ORDER OF THE REACTION WITH RESPECT TO REDUCING AMINO ACIDS IN THEIR OXIDATION BY N-BROMOSUCCINIMIDE IN PRESENCE OF IRIDIUM(III) CHLORIDE

In this chapter the main aim is to study the dependence of the title reactions on the concentration of reducing amino acids viz. glycine, alanine and valine. For this purpose, a set of experiments with varying concentrations of each of amino acid but at fixed concentrations of all other reactants have been carried out. Here all experiments have been conducted under isolation conditions i.e. concentration of N-bromo - succinimide has been kept comparatively lower than that of each of amino acid in each experiment. The kinetic data obtained in each experiments have been recorded in tables 4.1 - 4.6, 4.7 - 4.12 and 4.13 - 4.18. Here also the value of ($\frac{-dc}{dt}$) has been determined by usual method as described in the previous chapter. The data of tables 4.1 - 4.6, tables 4.7 - 4.12 and tables 4.13 - 4.18 are for oxidation of glycine, alanine and valine respectively.

TABLE 4.1

$[NBS] = 10.00 \times 10^{-4}$ M, $[Glycine] = 0.50 \times 10^{-2}$ M

$[HCl] = 4.00 \times 10^{-2}$ M, $[Ir(III)] = 4.80 \times 10^{-6}$ M

$[KCl] = 1.00 \times 10^{-2}$ M, $[Hg(OAc)_2] = 3.34 \times 10^{-3}$ M

Temperature 30°C

Time (min.)	ml of hypo (N/1000)	$[NBS]^* \times 10^4$ M	$\left(\frac{-dc}{dt}\right) \times 10^7$ M L^{-1} s^{-1}
00	10.78		
05	9.70		
10	9.28		
20	8.68		
30	8.18	9.00	1.12
45	7.48		
65	6.52		
85	5.74		
115	4.92		
140	4.00		

TABLE 4.2

$[NBS] = 10.00 \times 10^{-4}$ M, $[Glycine] = 0.67 \times 10^{-2}$ M

$[HCl] = 4.00 \times 10^{-2}$ M, $[Ir(III)] = 4.80 \times 10^{-6}$ M

$[KCl] = 1.00 \times 10^{-2}$ M, $[Hg(OAc)_2] = 3.34 \times 10^{-3}$ M

Temperature 30°C

Time (min.)	ml of hypo (M/1080)	$[NBS]^* \times 10^4$	$(\frac{-dc}{dt}) \times 10^7$ M l^{-1} s^{-1}
00	10.80		
05	10.26		
10	9.62		
20	8.86		
30	8.36	9.00	1.38
40	7.46		
55	6.70		
75	6.00		
100	4.90		
125	4.02		

TABLE 4.3

$[NBS] = 10.00\times10^{-4}$ M, $[Glycine] = 1.00\times10^{-2}$

$[HCl] = 4.00\times10^{-2}$ M, $[Ir(III)] = 4.80\times10^{-6}$ M

$[KCl] = 1.00\times10^{-2}$ M, $[Hg(OAc)_2] = 3.34\times10^{-3}$ M

Time (min.)	ml of hypo (N/1080)	$[NBS]^{*} \times 10^{7}$ M L^{-1} s^{-1}	$(\frac{-dc}{dt}) \times 10^{7}$ M l^{-1} s^{-1}
00	10.80		
05	10.02		
10	9.30		
20	8.26		
30	7.22	9.00	2.02
40	6.26		
60	4.90		
80	3.86		
100	3.02		

TABLE 4.4

$[NBS] = 10.00 \times 10^{-4}$ M, $[Glycine] = 1.33 \times 10^{-2}$ M

$[HCl] = 4.00 \times 10^{-2}$ M, $[Ir(III)] = 4.80 \times 10^{-6}$ M

$[KCl] = 1.00 \times 10^{-2}$ M, $[Hg(OAc)_2] = 3.34 \times 10^{-3}$ M

Temperature 30°C

Time (min.)	ml of hypo (N/1000)	$[NBS]^* \times 10^4$ M	$(\frac{-dc}{dt}) \times 10^7$ M l^{-1} s^{-1}
00	10.80		
05	10.22		
10	9.32		
20	8.04		
30	6.82	9.00	2.52
40	5.36		
50	4.82		
70	3.32		
90	2.70		

TABLE 4.5

[NBS] = 10.00×10^{-4} M, [Glycine] = 2.00×10^{-2} M

[HCl] = 4.00×10^{-2} M, [KCl] = 1.00×10^{-2} M

[Ir(III)] = 4.80×10^{-6} M, [Hg(OAc)$_2$] = 3.34×10^{-3} M

Temperature 30°C

Time (min.)	ml of hypo (M/1000)	$[NBS]^* \times 10^4$ M	$\left(\frac{-dc}{dt}\right) \times 10^7$ M l^{-1} s^{-1}
00	10.80		
05	9.54		
10	8.26		
20	6.48		
30	4.86	9.00	3.90
40	4.16		
50	3.36		
60	2.72		
75	2.00		
90	1.78		

TABLE 4.6

[NBS] = 10.00×10^{-4} M, [Glycine] = 4.00×10^{-2} M

[HCl] = 4.00×10^{-2} M, [Ir(III)] = 4.80×10^{-6} M

[KCl] = 1.00×10^{-2} M, [Hg(OAc)$_2$] = 3.34×10^{-3} M

Time (min.)	ml of hypo (M/1080)	[NBS]* $\times10^4$ M	$(\frac{-dc}{dt})\times10^{-7}$ M l^{-1} s^{-1}
00	10.80		
05	8.02		
10	6.04		
15	4.84	9.00	7.78
20	4.28		
25	3.72		
35	3.18		
40	3.02		
50	2.78		

TABLE 4.7

[NBS] = 10.00x10^{-4}M, [Alanine] = 0.60x10^{-2}M

[HCl] = 10.00x10^{-2}M, [KCl] = 1.00x10^{-2}M

[Ir(III)] = 4.80x10^{-6}M, [Hg(OAc)$_2$] = 3.34x10^{-3}M

Temperature 30°C

Time (min.)	ml of hypo (1/865)	[NBS]* x10^{4}M	($\frac{-dc}{dt}$)x10^7 M l^{-1} s^{-1}
00	8.64		
05	8.40		
10	8.28		
20	8.12		
40	7.68	9.00	0.36
70	7.08		
110	6.28		
180	4.76		
260	4.00		

TABLE 4.9

$[NBS] = 10.00\times10^{-4}M$, $[Alanine] = 0.67\times10^{-2}M$

$[HCl] = 10.00\times10^{-2}M$, $[KCl] = 1.00\times10^{-2}M$

$[Ir(III)] = 4.80\times10^{-6}M$, $[Hg(OAc)_2] = 3.34\times10^{-3}M$

Temperature $30^{o}C$

Time (min.)	ml of hypo (N/865)	$[NBS]^{*}\times10^{4}M$	$(\frac{-dc}{dt})\times10^{7}$ $M\ l^{-1}\ s^{-1}$
00	8.64		
05	8.48		
10	8.36		
20	8.10	9.00	0.56
30	7.60		
50	7.00		
70	6.66		
110	6.02		
180	4.92		
260	3.82		

TABLE 4.9

$[NBS] = 10.00 \times 10^{-4}$ M, $[Alanine] = 1.00 \times 10^{-2}$ M

$[HCl] = 10.00 \times 10^{-2}$ M, $[Ir(III)] = 4.80 \times 10^{-6}$ M

$[KCl] = 1.00 \times 10^{-2}$ M, $[Hg(OAc)_2] = 3.34 \times 10^{-3}$ M

Temperuture 30°C

Time (min.)	ml of hypo (N/865)	$[NBS]^* \times 10^4$ M	$(-\frac{dc}{dt}) \times 10^7$ M l^{-1} s^{-1}
00	8.64		
05	8.36		
10	8.28		
20	7.96		
40	7.28	9.00	0.70
70	6.24		
110	5.34		
180	4.38		
360	3.56		

TABLE 4.10

$[NBS] = 10.00 \times 10^{-4} M.$ $[Alanine] = 1.33 \times 10^{-2} M$

$[HCl] = 10.00 \times 10^{-2} M.$ $[KCl] = 1.00 \times 10^{-2} M$

$[I_r(III)] = 4.80 \times 10^{-6} M.$ $[Hg(OAc)_2] = 3.34 \times 10^{-3} M$

Temperature $30^{o}C$

Time (min.)	ml of hypo (M/865)	$[NBS]^{*}_{o} \times 10^{-4} M$	$(\frac{-dc}{dt}) \times 10^{7}$ $M\ l^{-1}\ s^{-1}$
00	8.64		
05	8.30		
10	7.96		
20	7.40		
40	6.52	9.00	0.92
70	5.74		
110	4.78		
190	3.66		
260	3.38		
315	3.10		

TABLE 4.11

$[NBS] = 10.00\times10^{-4}M$, $[Alanine] = 2000\times10^{-2}$

$[HCl] = 10.00\times10^{-2}M$, $[KCl] = 1.00\times10^{-2}M$

$[Ir(III)] = 4.80\times10^{-6}M$, $[Hg(OAc)_2] = 3.34\times10^{-3}M$,

Temperature 30^oC

Time (min.)	ml of hypo (M/865)	$[NBS]^* \times10^4$	$(\frac{-dc}{dt}) \times 10^7$ $M\ l^{-1}\ s^{-1}$
00	9.64		
05	8.18		
10	7.00		
20	6.96		
40	5.88	9.00	1.30
60	4.96		
90	4.12		
120	3.52		
150	3.02		

TABLE 4.12

$[NBS] = 10.00 \times 10^{-4}$ M, $[Alanine] = 4.00 \times 10^{-2}$ M

$[HCl] = 10.00 \times 10^{-2}$ M, $[KCl] = 1.00 \times 10^{-2}$ M

$[Ir(III)] = 4.80 \times 10^{-6}$ M $[Hg(OAc)_2] = 3.34 \times 10^{-3}$ M

Temperature 30°C

Time (min.)	ml of hypo (M/865)	$[NBS]^* \times 10^4$	$(\frac{-dc}{dt}) \times 10^7$ M l^{-1} s^{-1}
00	8.64		
05	7.44		
10	7.12		
20	6.08		
30	5.28	9.00	2.66
40	4.58		
60	3.82		
80	3.42		
110	3.02		

TABLE 4.13

[NBS] = 10.00×10^{-4} M, [Valine] = 1.00×10^{-2} M

[HCl] = 4.00×10^{-2} M, [KCl] = 1.00×10^{-2} M

[Ir(III)] = 4.80×10^{-6} M, [Hg(OAc)$_2$] = 3.34×10^{-3} M

Temperature 30°C

Time (min.)	ml of hypo (N/764)	$[\text{NBS}]^{*} \times 10^{4}$ M	$\left(\frac{-dc}{dt}\right) \times 10^{7}$ M l^{-1} s^{-1}
00	7.64		
05	7.22		
10	7.16		
20	7.00	9.00	0.56
40	6.52		
70	6.28		
110	5.12		
160	3.38		
200	2.68		

TABLE 4.14

$[NBS] = 10.00 \times 10^{-4}$ M. $[Valine] = 1.25 \times 10^{-2}$ M

$[HCl] = 4.00 \times 10^{-2}$ M. $[KCl] = 1.00 \times 10^{-2}$ M

$[Ir(III)] = 4.80 \times 10^{-6}$ M. $[Hg(OAc)_2] = 3.34 \times 10^{-3}$ M

Temperature $30^{\circ}C$

Time (min.)	ml of hypo (N/764)	$[NBS]^{\circ} \times 10^{4}$ M	$\left(\frac{-dc}{dt}\right) \times 10^{7}$ $M\ l^{-1}\ s^{-1}$
00	7.64		
05	7.50		
10	7.38		
20	7.00	9.00	0.74
40	6.68		
70	5.60		
110	4.50		
160	3.62		
220	2.80		

TABLE 4.15

[NBS] = 10.00×10^{-4} M, [Valine] = 1.67×10^{-2} M

[HCl] = 4.00×10^{-2} M, [KCl] = 1.00×10^{-2} M

[Ir(III)] = 4.80×10^{-6} M [$Hg(OAc)_2$] = 3.34×10^{-3} M

Temperature $30^{\circ}C$

Time (min.)	ml of hypo (N/764)	$[NBS]^* \times 10^4$ M	$\left(\frac{-dc}{dt}\right) \times 10^7$ M l^{-1} s^{-1}
00	7.64		
05	7.30		
10	7.16		
20	7.00		
40	6.28	9.00	0.84
70	5.12		
110	4.24		
160	3.20		
220	2.62		

TABLE 4.16

[NBS] = 10.00×10^{-4} M, [Valine] = 2.00×10^{-7}

[HCl] = 4.00×10^{-2} M, [KCl] = 1.00×10^{-2} M

[Ir(III)] = 4.80×10^{-6} M, [$Hg(OAc)_2$] = 3.34×10^{-3} M

Temperature 30°C

Time (min.)	ml of hypo (N/764)	[NBS]* $\times 10^4$ M	$\left(\frac{-dc}{dt}\right) \times 10^7$ M l^{-1} s^{-1}
00	7.64		
05	7.46		
10	7.18		
20	6.74	9.00	1.10
40	5.82		
70	4.90		
110	3.84		
160	2.88		
220	2.22		

TABLE 4.17

$[NBS] = 10.00 \times 10^{-4}$ M, $[Valine] = [illegible].50 \times 10^{-2}$ M

$[HCl] = 4.00 \times 10^{-2}$ M, $[KCl] = 1.00 \times 10^{-2}$ M

$[Ir(III)] = 4.80 \times 10^{-6}$ M, $[Hg(OAc)_2] = 3.34 \times 10^{-3}$ M

Temperature $30^{\circ}C$

Time (min.)	ml of hypo (N/764)	$[NBS]^{*} \times 10^{4}$ M	$\left(\frac{-dc}{dt}\right) \times 10^{7}$ M l^{-1} s^{-1}
00	7.64		
05	7.28		
10	6.96		
20	6.44		
40	5.72	9.00	1.25
60	4.78		
80	3.84		
100	3.42		
120	2.88		

TABLE 4.18

$[NBS] = 10.00 \times 10^{-4}M$, $[Valine] = 5.00 \times 10^{-2}M$

$[HCl] = 4.00 \times 10^{-2}M$, $[KCl] = 1.00 \times 10^{-2}M$

$[Ir(III)] = 4.80 \times 10^{-6}M$, $[Hg(OAc)_2] = 3.34 \times 10^{-3}M$

Temperature $30^{\circ}C$

Time (min.)	ml of hypo (N/764)	$[NBS]^{*} \times 10^{4}M$	$(\frac{-dc}{dt}) \times 10^{7}$ $M\ l^{-1}\ s^{-1}$
00	7.64		
05	7.00		
10	6.52		
20	5.60	9.00	2.52
30	4.92		
40	4.22		
50	3.84		
70	3.16		
100	2.86		

The kinetic results of tables 4.1 - 4.6, 4.7-4.12 and 4.13 - 4.18 have been summarised in tables 4.19, 4.20 and 4.21 respectively.

TABLE 4.19

$[NBS] = 10.00 \times 10^{-4}$ M, $[HCl] = 4.00 \times 10^{-2}$ M

$[Ir(III)] = 4.80 \times 10^{-6}$ M, $[KCl] = 1.00 \times 10^{-2}$ M

$[Hg(OAc)_2] = 3.34 \times 10^{-3}$ M and Temperature 30°C

$[Glycine] \times 10^2$ M	$(\frac{-dc}{dt}) \times 10^7$ M L^{-1} s^{-1}	$10^4 k_1 = \frac{(-dc/dt)}{[NBS]^*}$ s^{-1}	$10^2 k_2 = \frac{k_1}{[Glycine]}$ M^{-1} l^{+1} s^{-1}
0.50	1.12	1.24	2.48
0.67	1.38	1.53	2.28
1.00	2.02	2.24	2.24
1.33	2.52	2.80	2.11
2.00	3.90	4.33	2.17
4.00	[illegible]	8.64	2.16
4.00			

$[NBS]^* = 9.00 \times 10^{-4}$ M (at which $(^{-dc}/_{dt})$ was determined

Average $k_2 = 2.24 \times 10^{-2}$ M^{-1} l^{+1} s^{-1}

TABLE 4.20

$[NBS] = 10.00 \times 10^{-4}$ M,   HCl $= 10.00 \times 10^{-2}$ M

$[KCl] = 1.00 \times 10^{-2}$ M,   Ir(III) $= 4.80 \times 10^{-6}$ M

$[Hg(OAc)_2] = 3.34 \times 10^{-3}$ M,   Temperature 30°C

[Alanine] $\times 10^2$ M	$\left(\frac{-dc}{dt}\right) \times 10^7$ M l^{-1} s^{-1}	$10^4 k_1 = \frac{(-dc/dt)}{[NBS]^*}$ s^{-1}	$10^2 k_2 = \frac{k_1}{[Alanine]}$ M^{-1} l^{+1} s^{-1}
0.50	0.36	0.40	0.80
0.67	0.56	0.62	0.92
1.00	0.70	0.78	0.78
1.33	0.92	1.02	0.77
2.00	1.38	1.53	0.77
4.00	2.66	2.95	0.74

$[NBS]^* = 9.00 \times 10^{-4}$ M at which $\left(\frac{-dc}{dt}\right)$ was determined

Average $k_2 = 0.79 \times 10^{-2}$ M^{-1} l^{+1} s^{-1}

TABLE 4.21

[NBS] = 10.00×10^{-4}M, [HCl] = 4.00×10^{-2}M

[KCl] = 1.00×10^{-2}M, [Ir(III)] = 4.90×10^{-6}M

[Hg(OAc)$_2$] = 3.34×10^{-3}M, Temperature 30°C

[Valine]$\times10^2$ M	$\left(\frac{-dc}{dt}\right)\times10^7$ M $l^{-1}s^{-1}$	$10^4k_1 = \frac{\left(\frac{-dc}{dt}\right)}{[NBS]^*}$ s^{-1}	$10^2k_2 = \frac{k_1}{[Valine]}$ $M^{-1}l^{+1}s^{-1}$
1.00	0.56	0.62	0.62
1.25	0.74	0.82	0.65
1.67	0.84	0.93	0.56
2.00	1.10	1.22	0.61
2.50	1.25	1.39	0.56
5.00	2.52	2.80	0.56

$[NBS]^* = 9.00\times10^{-4}$M at which $\left(\frac{-dc}{dt}\right)$ was determined

Average $k_2 = 0.59\times10^{-2}M^{-1}l^{+1}s^{-1}$

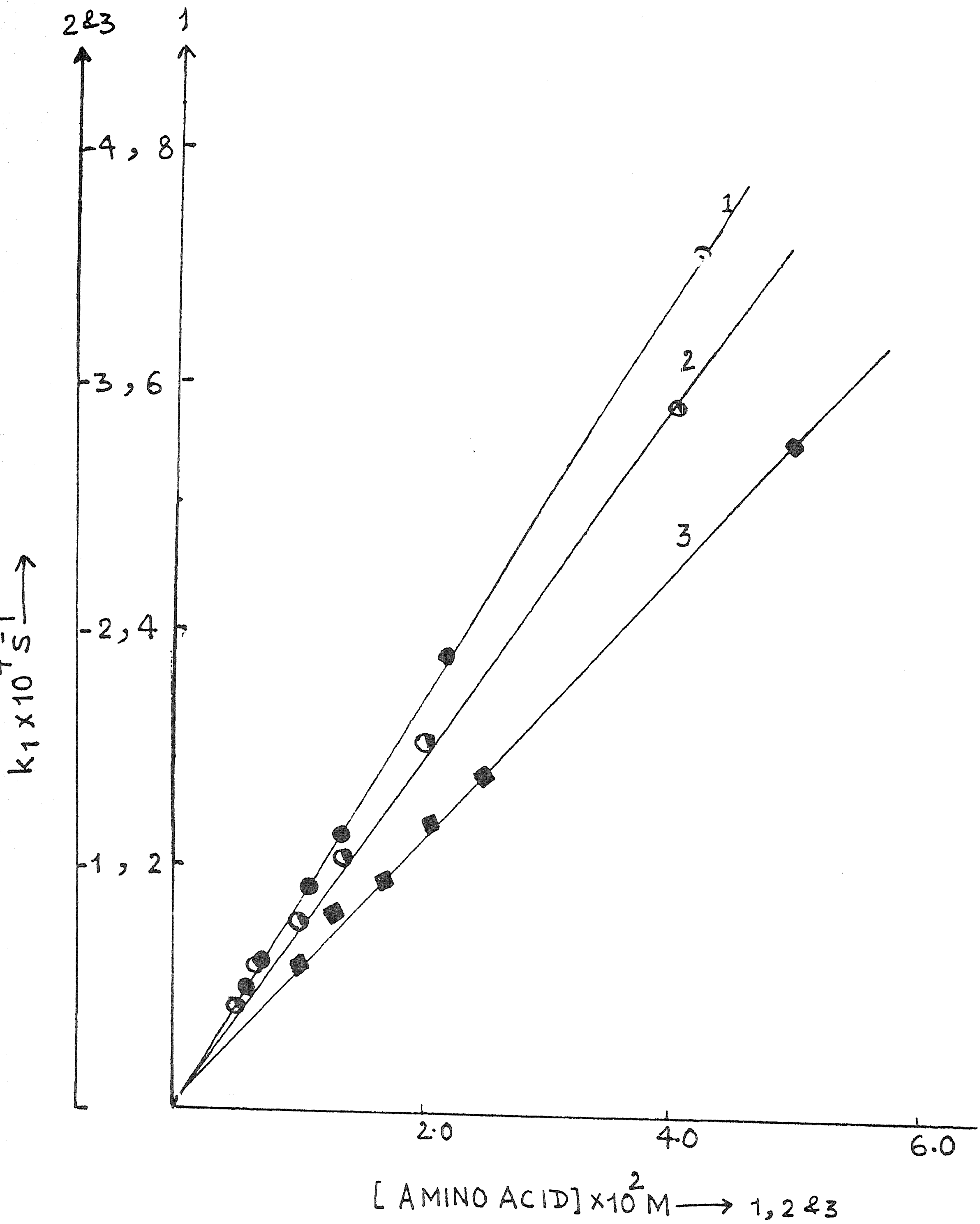

Fig. 4.1 : Plot between k_1 and [Amino acid]

(1) → GLYCINE under the conditions of Table 4.19.

(2) → ALAnine under the conditions of Table 4.20.

(3) → VALINE under the conditions of Table 4.21.

When kinetic data of tables 4.19, 4.20 and 4.21 obtained in oxidation of glycine, alanine and valine are examined carefully, it is observed that on increasing the concentration of these amino acids the value of ($\frac{-dc}{dt}$) and k_1 increase linearly which indicates that oxidation of these amino acids follow first order dependence on the concentration of each amino acid i.e. glycine, alanine and valine.

The above observation regarding first - order kinetics in amino acids is, further, confirmed by plotting a graph between k_1 values and [amino acids]. A straight line in oxidation of each amino acid is obtained (Fig.4.1). The slope of each curve gives the value of k_2. The graphical k_2 value thus obtained is close to average value of k_2 recorded in the bottom of tables 4.19, 4.20 and 4.21. The closeness in k_2 values obtained from tables 4.19, 4.20 and 4.21 and graph of Fig. 4.1 clearly confirms first - order kinetics in amino acid.

CHAPTER V

COMPUTATION OF ORDER OF REACTION WITH RESPECT OF HYDROCHLORIC ACID IN NBS - AMINO ACIDS SYSTEM WITH Ir(III) AS CATALYST

5 : COMPUTATION OF DEPENDENCE OF Ir(III) CATALYSED OXIDATION OF AMINO ACIDS BY N-BROMOSUCCINIMIDE ON HYDROCHLORIC ACID

This chapter describes the dependence of the reactions (involving N-bromosuccinimide as oxidant and each of glycine, alanine and valine as reductants in the presence of iridium(III) chloride as catalyst) on hydrochloric acid. In order to obtain this aim, a series of experiments with varying concentrations of hydrochloric acid at fixed concentrations of all other reactants in oxidation of each of amino acids are done. The results of such experiments have been recorded in tables 5.1 - 5.6, 5.7 - 5.12 and 5.13 - 5.18 in oxidation of glycine, alanine and valine. Here also all experiments have been carried out under isolation conditions. The value of ($\frac{-dc}{dt}$) here also has been determined by usual method as described in 3rd chapter. Although on changing the concentration of HCl, the value of ionic strength of the medium also changes. Since preliminary investigations have indicated negligible effect of ionic strength of the medium on the reaction rate. Hence no effort was made to keep ionic strength of the medium constant.

TABLE 5.1

$[NBS] = 10.00 \times 10^{-4} M,$ $[Glycine] = 2.00 \times 10^{-2} M$

$[HCl] = 2.50 \times 10^{-2} M,$ $[Ir(III)] = 4.80 \times 10^{-6} M$

$[KCl] = 1.00 \times 10^{-2} M,$ $[Hg(OAc)_2] = 3.34 \times 10^{-3} M$

Temperature $30^{\circ}C$

Time (min.)	ml of hypo (M/1120)	$[NBS]^{*} \times 10^{4} M$	$\left(\frac{-dc}{dt}\right) \times 10^{7}$ $M\ l^{-1}\ s^{-1}$
00	11.20		
05	9.86		
10	8.48		
15	7.72		
20	7.02	9.00	3.88
30	6.00		
40	5.06		
60	4.08		
80	3.72		

TABLE 5.2

$[NBS] = 10.00 \times 10^{-4} M$, $[Glycine] = 1.00 \times 10^{-2} M$

$[HCl] = 4.00 \times 10^{-2} M$, $[Ir(III)] = 4.80 \times 10^{-6} M$

$[KCl] = 1.00 \times 10^{-2} M$, $[Hg(OAc)_2] = 3.34 \times 10^{-3} M$

Temperature $30^{\circ}C$

Time (min.)	ml of hypo (N/1120)	$[NBS]^{*} \times 10^{4}$	$\left(\frac{-dc}{dt}\right) \times 10^{7}$ $M\ l^{-1}\ s^{-1}$
00	11.20		
05	10.10		
10	9.20		
20	7.84		
30	6.98	9.00	2.52
40	5.98		
50	5.28		
60	4.72		
80	4.28		

TABLE 5.3

[NBS] = 10.00×10^{-4} M, [Glycine] = 2.00×10^{-2} M

[HCl] = 5.00×10^{-2} M, [Ir(III)] = 4.80×10^{-6} M

[KCl] = 1.00×10^{-2} M, [Hg(OAc)$_2$] = 3.34×10^{-3} M

Temperature 30°C

Time (min.)	ml of hypo (N/1120)	$[NBS]^* \times 10^4$	$\left(\frac{-dc}{dt}\right) \times 10^7$ M l^{-1} s^{-1}
00	11.20		
05	10.52		
10	9.52		
20	8.32		
30	7.08	9.00	2.22
50	5.68		
70	4.84		
90	4.42		
110	4.28		

TABLE 5.4

$[NBS] = 10.00\times10^{-4}$ M, $[Glycine] = 2.00\times10^{-2}$ M

$[HCl] = 6.67\times10^{-2}$ M, $[Ir(III)] = 4.80\times10^{-6}$ M

$[KCl] = 1.00\times10^{-2}$ M, $[Hg(OAc)_2] = 3.34\times10^{-3}$ M

Temperature 30°C

Time (min.)	ml of hypo (M/1120)	$[NBS]^{*}\times10^{4}$ M	$\left(\frac{-dc}{dt}\right)\times10^{7}$ M l^{-1} s^{-1}
00	11.20		
05	10.70		
10	9.84		
20	8.66		
40	6.68	9.00	2.06
60	5.72		
80	4.64		
100	4.30		
120	3.90		

TABLE 5.5

[NBS] = 10.00×10^{-4} M, [Glycine] = 2.00×10^{-2} M

[HCl] = 10.00×10^{-2} M, [Ir(III)] = 4.80×10^{-6} M

[KCl] = 1.00×10^{-2} M, [$Hg(OAc)_2$] = 3.34×10^{-3} M

Temperature 30°C

Time (min.)	ml of hypo (N/1120)	[NBS]* $\times 10^{4}$ M	$\left(\frac{-dc}{dt}\right) \times 10^{7}$ M $l^{-1} s^{-1}$
00	11.20		
05	10.78		
10	10.10		
20	9.20		
30	8.60	9.00	1.32
60	6.52		
90	5.36		
120	4.72		
150	4.22		

TABLE 5.6

[NBS] = 10.00×10^{-4} M, [Glycine] = 2.00×10^{-2} M

[HCl] = 13.33×10^{-2} M, [Ir(III)] = 4.80×10^{-6} M

[KCl] = 1.00×10^{-2} M , [Hg(OAc)$_2$] = 3.34×10^{-3} M

Temperature 30°C

Time (min.)	ml of hypo (M/1120)	[NBS]* $\times 10^{4}$ M	$\left(\frac{-dc}{dt}\right) \times 10^{7}$ M l^{-1} s^{-1}
00	11.20		
05	10.98		
10	10.56		
20	9.86		
40	8.76	9.00	0.84
70	7.30		
100	6.20		
130	5.36		
160	4.54		

TABLE 5.7

[NBS] = 10.00×10^{-4} M, [Alanine] = 2.00×10^{-2} M

[HCl] = 2.50×10^{-2} M , [Ir (III)] = 4.80×10^{-6} M

[KCl] = 1.00×10^{-2} M , [Hg (OAc)$_2$] = 3.34×10^{-3} M

Temperature 30^{o}C

Time (min.)	ml of hypo (M/820)	[NBS]* x10^{4} M	($\frac{-dc}{dt}$)x10^{7} M l^{-1} s^{-1}
00	8.20		
05	7.42		
10	7.08		
20	6.02		
30	5.48	9.00	2.26
40	4.70		
50	4.14		
65	3.48		
95	2.50		

TABLE 5.8

$[NBS] = 10.00 \times 10^{-4} M$, $[Alanine] = 2.00 \times 10^{-2} M$

$[HCl] = 4.00 \times 10^{-2} M$, $[Ir(III)] = 4.80 \times 10^{-6} M$

$[KCl] = 1.00 \times 10^{-2} M$, $[Hg(OAc)_2] = 3.34 \times 10^{-3} M$

Temperature 30°C

Time (min.)	ml of hypo (M/820)	$[NBS]^* \times 10^4$	$(\frac{-dc}{dt}) \times 10^7$ M l^{-1} s^{-1}
00	8.20		
05	7.52		
10	6.80		
20	6.40	9.00	1.94
40	4.80		
60	3.62		
80	3.28		
100	2.48		
120	2.00		

TABLE 5.9

[NBS] = 10.00x10^{-4}M, [Alanine] = 2.00x10^{-2}M

[HCl] = x10^{-2}M, [Ir(III)] = 4.80x10^{-6}M

[KCl] = 1.00x10^{-2} M, [Hg(OAc)$_2$] = 3.34x10^{-3}M

Temperature 30^{o}C

Time (min.)	ml of hypo (M/820)	[NBS]*x10^{4}M	$(-\frac{dc}{dt})$x10^{7} M l^{-1} s^{-1}
00	8.20		
05	7.76		
10	7.50		
20	6.74		
40	5.42	9.00	1.62
80	3.62		
100	3.42		
120	2.74		

TABLE 5.10

[NBS] = 10.00×10^{-4} M, [Alanine] = 2.00×10^{-2} M

[HCl] = 6.67×10^{-2} M, [Ir(III)] = 4.80×10^{-6} M

[KCl] = 1.00×10^{-2} M, [Hg(OAc)2] = 3.34×10^{-3} M

Temperature 30°C

Time (min.)	ml of hypo (N/820)	[NBS]* $\times 10^{4}$ M	$\left(\frac{-dc}{dt}\right) \times 10^{7}$ M l^{-1} s^{-1}
00	8.20		
05	7.80		
10	7.60		
20	6.92	9.00	1.46
40	5.60		
70	4.04		
100	3.34		
130	2.72		
160	2.56		

TABLE 5.11

[NBS] = 10.00×10^{-4} M. [Alanine] = 2.00×10^{-2} M

[HCl] = 10.00×10^{-2} M. [Ir(III)] = 4.80×10^{-6} M

[KCl] = 1.00×10^{-2} M. [Hg(OAc)$_2$] = 3.34×10^{-3} M

Temperature 30°C

Time (min.)	ml of hypo (M/820)	$[NBS]^{*} \times 10^{4}$ M	$\left(\frac{-dc}{dt}\right) \times 10^{7}$ M l^{-1} s^{-1}
00	8.20		
05	8.04		
10	7.64		
20	7.08		
40	6.08	9.00	1.06
70	4.94		
100	4.12		
130	3.22		
160	2.92		

TABLE 5.12

[NBS] = 10.00×10^{-4} M, [Alanine] = 2.00×10^{-2} M

[HCl] = 13.33×10^{-2} M, [I_r(III)] = 4.80×10^{-6} M

[KCl] = 1.00×10^{-2} M, [Hg(OAc)$_2$] = 3.34×10^{-3} M

Temperature 30°C

Time (min.)	ml of hypo (N/820)	$[NBS]^* \times 10^4$ M	$\left(\frac{-dc}{dt}\right) \times 10^7$ M l^{-1} s^{-1}
00	8.20		
05	8.08		
10	7.84		
20	7.42	9.00	0.82
40	6.32		
70	5.34		
100	4.36		
130	3.56		
160	2.70		

TABLE 5.13

[NBS] = 10.00×10^{-4} M, [Valine] = 2.00×10^{-2} M

[HCl] = 2.50×10^{-2} M, [I_r(III)] = 4.80×10^{-6} M

[KCl] = 1.00×10^{-2} M, [Hg(OAc)$_2$] = 3.34×10^{-3} M

Temperature 30°C

Time (min.)	ml of hypo (N/800)	$[NBS]^{*}\times10^{4}$ M	$(\frac{-dc}{dt})\times10^{7}$ M l^{-1} s^{-1}
00	8.20		
05	7.44		
10	7.06		
20	6.04		
30	5.50		
40	4.72	9.00	2.28
50	4.14		
66	3.46		
95	2.50		

TABLE 5.14

[NBS] = 10.00×10^{-4} M, [Valine] = 2.00×10^{-2} M

[HCl] = 4.00×10^{-2} M, [Ir(III)] = 4.80×10^{-6} M

[KCl] = 1.00×10^{-2} M, [$Hg(OAc)_2$] = 3.34×10^{-3} M

Temperature 30°C

Time (min.)	ml of hypo (N/820)	[NBS]* $\times 10^{4}$ M	$(-\frac{dc}{dt}) \times 10^{7}$ M l^{-1} s^{-1}
00	8.20		
05	7.50		
10	6.86		
20	6.34		
30	5.60	9.00	1.94
40	4.80		
50	3.64		
80	3.26		
100	2.50		
120	2.00		

TABLE 5.15

$[NBS] = 10.00\times10^{-4}M$, $[Valine] = 2.00\times10^{-2}M$

$[HCl] = 5.00\times10^{-2}M$, $[Ir(III)] = 4.80\times10^{-6}M$

$[KCl] = 1.00\times10^{-2}M$, $[Hg(OAc)_2] = 3.34\times10^{-3}M$

Temperature $30^{\circ}C$

Time (min.)	ml of hypo (N/820)	$[NBS]^{*}\times10^{4}M$	$(\frac{-dc}{dt})\times10^{7}$ $M\ l^{-1}\ s^{-1}$
00	8.20		
05	7.74		
10	7.46		
20	6.74		
40	5.44	9.00	1.64
60	4.06		
80	3.62		
100	3.42		
120	2.78		

TABLE 5.16

[NBS] = 10.00×10^{-4} M, [Valine] = 2.00×10^{-2} M

[HCl] = 6.67×10^{-2} M, [I_r(III)] = 4.80×10^{-6} M

[KCl] = 1.00×10^{-2} M, [Hg(OAc)$_2$] = 3.34×10^{-3} M

Temperature 30°C

Time (min.)	ml of hypo (N/820)	[NBS]* $\times 10^4$ M	$\left(\frac{-dc}{dt}\right) \times 10^7$ M l^{-1} s^{-1}
00	8.20		
05	7.78		
10	7.60		
20	6.90		
40	5.60	9.00	1.46
70	4.04		
100	3.34		
130	2.72		
160	2.56		

TABLE 5.17

[NBS] = 10.00×10^{-4} M.   [Valine] = 2.00×10^{-2} M

[HCl] = 10.00×10^{-2} M.   [Ir(III)] = 4.80×10^{-6} M

[KCl] = 1.00×10^{-2} M.   [Hg(OAc)$_2$] = 3.34×10^{-3} M

Temperature 30°C

Time (min.)	ml of hypo (N/820)	[NBS]*x10^4	$\left(\frac{-dc}{dt}\right)\times10^7$ M l^{-1} s^{-1}
00	8.20		
05	8.02		
10	7.64		
20	7.08		
40	6.04	9.00	1.06
70	4.94		
100	4.08		
130	3.22		
160	2.92		

TABLE 5.18

$[NBS] = 10.00 \times 10^{-4}$ M, $[Valine] = 2.00 \times 10^{-2}$ M

$[HCl] = 13.33 \times 10^{-2}$ M, $[Ir(III)] = 4.80 \times 10^{-6}$ M

$[KCl] = 1.00 \times 10^{-2}$ M, $[Hg(OAc)_2] = 3.34 \times 10^{-3}$ M

Temperature 30°C

Time (min.)	ml of hypo (M/820)	$[NBS]^* \times 10^4$ M	$\left(\frac{-dc}{dt}\right) \times 10^7$ M l^{-1} s^{-1}
00	8.2		
05	8.04		
10	7.84		
20	7.42		
40	6.32	9.00	0.80
70	5.36		
100	4.34		
130	5.56		
160	2.66		

The kinetic results recorded in tables 5.1 - 5.6, 5.7 - 5.12 and 5.13 - 5.18 have been summarised in tables 5.19, 5.20 and 5.21 respectively.

TABLE 5.19

[NBS] = 10.00×10^{-4} M, [Glycine] = 2.00×10^{-2} M

[KCl] = 1.00×10^{-2} M, [Ir(III)] = 4.80×10^{-6} M

[Hg(OAc)$_2$] = 3.34×10^{-3} M, Temperature 30°C

[HCl] x 10^2 M	($\frac{-dc}{dt}$)x10^7 M l^{-1} s^{-1}	k_1 x 10^4 s^{-1}
2.50	3.88	4.31
4.00	2.52	2.80
5.00	2.22	2.47
6.67	2.06	2.30
10.00	1.32	1.47
13.33	0.84	0.93

[NBS]* = 9.00×10^{-4} M at which ($^{-dc}/_{dt}$) was determined

TABLE 5.20

[NBS] = 10.00×10^{-4} M, [Alanine] = 2.00×10^{-2} M

[KCl] = 1.00×10^{-2} M, [Ir(III)] = 4.80×10^{-6} M

[$Hg(OAc)_2$] = 3.34×10^{-3} M, Temperature 30^{o}C

[HCl] x 10^2 M	$(\frac{-dc}{dt})\times10^7$ M l^{-1} s^{-1}	$k_1\times10^4$ s^{-1}
2.50	2.26	2.51
4.00	1.94	2.15
5.00	1.62	1.80
6.67	1.46	1.62
10.00	1.06	1.18
13.33	0.82	0.91

[NBS]* = 9.00×10^{-4} M at which $(\frac{-dc}{dt})$ was determined

TABLE 5.21

[NBS] = 10.00x10^{-4}M, [Valine] = 2.00x10^{-2}M

[KCl] = 1.00x10^{-2}M , [Ir(III)] = 4.80x10^{-6}M

$Hg(OAc)_2$ = 3.34x10^{-3}M, Temperature 30^{o}C

[HCl]x 10^2 M	($\frac{-dc}{dt}$)x10^7 M l^{-1} s^{-1}	k_1 x 10^4 s^{-1}
2.50	2.20	2.53
4.00	1.94	2.15
5.00	1.64	1.82
6.67	1.46	1.62
10.00	1.06	1.18
13.33	0.80	0.89

[NBS]* = 9.00 x 10^{4}M at which ($\frac{-dc}{dt}$) was plotted

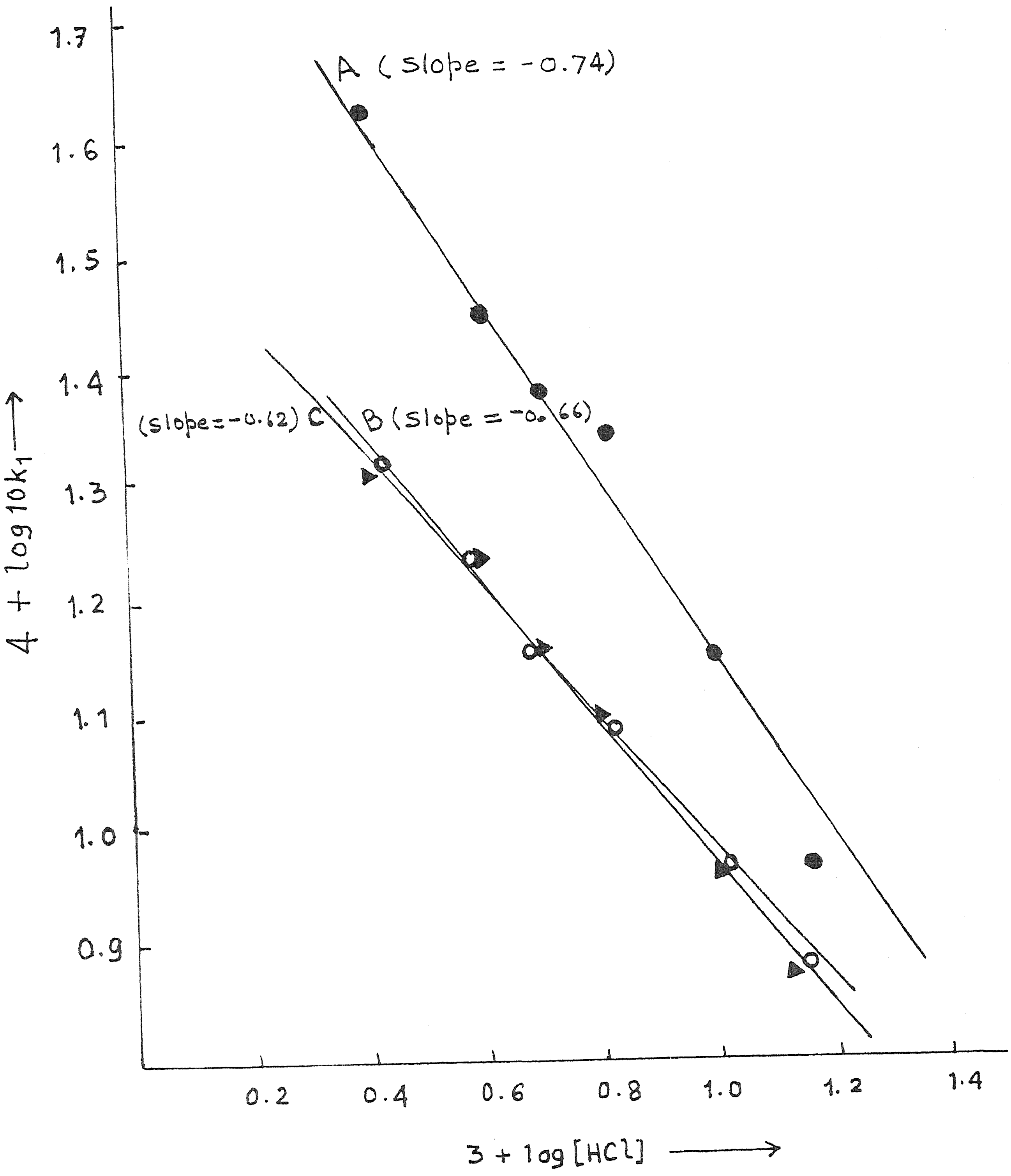

Fig. 5.1 : Plot between log k_1 and log [HCl]

A → GLYCINE : under the conditions of TABLE 5.19.

B → ALANINE : under the conditions of TABLE 5.20.

C → VALINE : under the conditions of TABLE 5.21.

It is quite clear from the data of summarised tables 5.19, 5.20 and 5.21 that the first - order rate constant decreases on increasing the concentration of hydrochloric acid in oxidation of each of glycine, alanine and valine by N-bromosuccinimide. This indicates that order of the aforesaid redox systems with respect to hydrochloric acid is negative fractional as no relationship is observed between [HCl] and k_1.

Further, the above experimental finding as regards to order in HCl is confirmed by graphical method on plotting log k_1 against log HCl in each amino acid oxidations (fig. 5.1A, 5.1B and 5.1C). A straight line with negative fractional slope is observed in each graph. This confirms that order in HCl is negative fractional in oxidation of glycine, alanine and valine.

CHAPTER VI

COMPUTATION OF ORDER OF REACTION WITH RESPECT TO Ir(III) IN NBS - AMINO ACIDS REDOX SYSTEM IN HYDROCHLORIC ACID MEDIA

6 : COMPUTATION OF ORDER OF REACTION WITH RESPECT TO IRIDIUM (III) CHLORIDE IN OXIDATION OF AMINO ACIDS BY ACIDIC SOLUTION OF N-BROMOSUCCINIMIDE

Iridium (III) chloride has been used here in this redox system as homogeneous catalyst. In this chapter an attempt has been made to determine the order of the reaction with respect to I_r(III) in all redox systems involving N-bromosuccinimide as oxidant and glycine, alanine and valine as reducing substances. For this purpose a number of experiments with different concentrations of I_r(III) but at fixed concentrations of all other reactants in oxidation of each amino acids have been carried out and the results of such experiments have been recorded in tables 6.1 - 6.6, 6.7 - 6.12 and 6.13 - 6.18 in oxidation of glycine, alanine and valine respectively. Here ($\frac{-dc}{dt}$) values in each case have been determined as usual as described in 3rd chapter.

TABLE 6.1

[NBS] = 20.00×10^{-4} M. [Ir(III)] = 0.60×10^{-6} M

[HCl] = 4.00×10^{-2} M. [Glycine] = 4.00×10^{-2} M

[KCl] = 1.00×10^{-2} M. [$Hg(OAc)_2$] = 3.34×10^{-3} M

Temperature 30°C

Time (min.)	ml of hypo (M/490)	$[NBS]^* \times 10^4$	$(\frac{-dc}{dt}) \times 10^7$ M l^{-1} s^{-1}
00	9.76		
20	8.62		
40	7.94		
80	6.86		
120	5.84	18.40	1.08
160	5.06		
240	3.90		
320	3.12		
400	2.54		

TABLE 6.2

$[NBS] = 20.00 \times 10^{-4} M,$ $[Ir(III)] = 1.20 \times 10^{-6} M$

$[HCl] = 4.00 \times 10^{-4} M,$ $[Glycine] = 4.00 \times 10^{-6} M$

$[KCl] = 1.00 \times 10^{-2} M,$ $[Hg(OAc)_2] = 3.34 \times 10^{-3} M$

Temperature $30^{\circ}C$

Time (min.)	ml of hypo (M/490)	$[NBS]^{*} \times 10^{4} M$	$(\frac{-dc}{dt}) \times 10^{7}$ $M\ l^{-1}\ s^{-1}$
0	9.76		
10	8.64		
20	7.96		
40	6.82	18.40	2.10
60	5.82		
80	5.04		
120	3.92		
160	3.10		
200	2.56		

TABLE 6.3

[NBS] = 20.00×10^{-4} M, [Ir(III)] = 1.00×10^{-6} M

[HCl] = 4.00×10^{-2} M, [Glycine] = 4.00×10^{-2} M

[KCl] = 1.00×10^{-2} M, [$Hg(OAc)_2$] = 3.34×10^{-3} M

Temperature 30°C

Time (min.)	ml of hypo (N/490)	$[NBS]^{*}\times10^{4}$ M	$\left(\frac{-dc}{dt}\right)\times10^{7}$ M l^{-1} s^{-1}
00	9.76		
10	8.24		
20	7.54		
40	6.38		
60	5.42	18.40	3.32
80	4.82		
120	3.62		
160	2.80		
200	2.36		

TABLE 6.4

$[NBS] = 20.00 \times 10^{-4}M$, $[Ir(III)] = 2.40 \times 10^{-6}M$

$[HCl] = 4.00 \times 10^{-2}M$, $[Glycine] = 4.00 \times 10^{-2}M$

$[KCl] = 1.00 \times 10^{-2}M$, $[Hg(OAc)_2] = 3.34 \times 10^{-3}M$

Temperature $30^{\circ}C$

Time (min.)	ml of hypo (N/490)	$[NBS]^{*} \times 10^{4}M$	$(\frac{-dc}{dt}) \times 10^{7}$ $M\ l^{-1}\ s^{-1}$
00	0.76		
10	8.00		
20	7.12		
40	6.08	18.40	4.14
60	5.16		
80	4.62		
120	3.40		
140	3.00		
160	2.44		

TABLE 6.5

$[NBS] = 20.00 \times 10^{-4}$ M, $[Glycine] = 4.00 \times 10^{-2}$ M

$[HCl] = 4.00 \times 10^{-2}$ M, $[I_2(XII)] = 3.60 \times 10^{-6}$ M

$[KCl] = 1.00 \times 10^{-2}$ M, $[Hg(OAc)_2] = 3.34 \times 10^{-3}$ M

Temperature 30°C

Time (min.)	ml of hypo (N/490)	$[NBS]^* \times 10^4$ M	$(\frac{-dc}{dt}) \times 10^7$ M l^{-1} s^{-1}
00	9.76		
05	8.26		
10	7.52		
20	6.40		
30	5.40	10.40	6.56
40	4.86		
60	3.60		
80	2.82		
100	2.40		

TABLE 6.6

$[NBS] = 20.00 \times 10^{-4}$ M, $[Glycine] = 2.00 \times 10^{-2}$ M

$[HCl] = 4.00 \times 10^{-2}$ M, $[Ir(III)] = 5.40 \times 10^{-6}$ M

$[KCl] = 1.00 \times 10^{-2}$ M, $[Hg(OAc)_2] = 3.34 \times 10^{-3}$ M

Temperature 30°C

Time (min.)	ml of hypo (M/490)	$[NBS]^{*} \times 10^{4}$ M	$\left(\frac{-dc}{dt}\right) \times 10^{7}$ M l^{-1} s^{-1}
00	9.76		
05	8.02		
10	7.28		
20	6.02		
30	5.04	18.40	9.82
40	4.56		
50	3.88		
60	3.26		
80	2.68		

TABLE 6.7

$[NBS] = 20.00\times10^{-4}$ M, $[I_r(III)] = 0.60\times10^{-6}$ M

$[HCl] = 10.00\times10^{-2}$ M, $[Alanine] = 4.00\times10^{-2}$ M

$[KCl] = 1.00\times10^{-2}$ M, $[Hg(OAc)_2] = 3.36\times10^{-3}$ M

Temperature 30°C

Time (min.)	ml of hypo (N/430)	$[NBS]^{*}\times10^{4}$ M	$(\frac{-dc}{dt})\times10^{7}$ M l^{-1} s^{-1}
00	8.56		
20	8.14		
40	7.86		
160	6.52	19.00	0.65
280	5.22		
400	4.62		
500	4.28		
600	3.66		

TABLE 6.8

$[NBS] = 20.00 \times 10^{-4}$ M, $[I_r(III)] = 1.20 \times 10^{-6}$ M

$[HCl] = 10.00 \times 10^{-2}$ M, [Alanine] $= 4.00 \times 10^{-2}$ M

$[KCl] = 1.00 \times 10^{-2}$ M, $[Hg(OAc)_2] = 3.34 \times 10^{-3}$ M

Temperature 30°C

Time (min.)	ml of hypo (N/430)	$[NBS]^* \times 10^4$ M	$\left(\frac{-dc}{dt}\right) \times 10^7$ M l^{-1} s^{-1}
00	8.56		
10	8.16		
20	7.90		
40	7.24		
80	6.56	19.00	1.26
140	5.30		
200	4.68		
260	4.36		
320	3.70		

TABLE 6.9

$[NBS] = 20.00 \times 10^{-4}$ M, $[I_r(III)] = 1.80 \times 10^{-6}$ M

$[HCl] = 10.00 \times 10^{-2}$ M, $[Alanine] = 4.00 \times 10^{-2}$ M

$[KCl] = 1.00 \times 10^{-2}$ M, $[Hg(OAc)_2] = 3.34 \times 10^{-3}$ M

Temperature 30°C

Time (min.)	ml of hypo (N/430)	$[NBS]^* \times 10^4$ M	$(\frac{-dc}{dt}) \times 10^7$ M l^{-1} s^{-1}
00	8.56		
10	7.96		
20	7.68		
40	7.00		
60	6.56	19.00	1.94
80	6.24		
100	5.52		
140	4.92		
200	4.34		

TABLE 6.10

$[NBS] = 20.00 \times 10^{-4} M$, $[I_r(III)] = 2.40 \times 10^{-6} M$

$[HCl] = 10.00 \times 10^{-2} M$, $[Alanine] = 4.00 \times 10^{-2} M$

$[KCl] = 1.00 \times 10^{-2} M$, $[Hg(OAc)_2] = 3.34 \times 10^{-3} M$

Temperature 30°C

Time (min.)	ml of hypo (N/420)	$[NBS]^* \times 10^4 M$	$(\frac{-dc}{dt}) \times 10^7$ $M\,l^{-1}\,s^{-1}$
00	8.56		
05	8.18		
10	7.92		
20	7.30	19.00	2.56
40	6.58		
70	5.32		
100	4.62		
130	4.38		
160	3.76		

TABLE 6.11

[NBS] = 20.00×10^{-4} M, [Alanine] = 4.00×10^{-2} M

[HCl] = 10.00×10^{-2} M, [I_r(III)] = 3.60×10^{-6} M

[KCl] = 1.00×10^{-2} M, [$Hg(OAc)_2$] = 3.34×10^{-3} M

Temperature 30^{0}C

Time (min.)	ml of hypo (N/430)	[NBS]* $\times 10^{4}$ M	$(\frac{-dc}{dt}) \times 10^{7}$ M l^{-1} s^{-1}
00	8.56		
05	7.88		
10	7.68		
20	7.02	19.00	3.82
40	6.28		
70	5.06		
100	4.26		
130	4.00		
160	3.60		

TABLE 6.12

$[NBS] = 20.00 \times 10^{-4} M$, $[Alanine] = 4.00 \times 10^{-2} M$

$[HCl] = 10.00 \times 10^{-2} M$, $[Ir(III)] = 5.40 \times 10^{-6} M$

$[KCl] = 1.00 \times 10^{-2} M$, $[Hg(OAc)_2] = 3.34 \times 10^{-3} M$

Temperature $30^{\circ}C$

Time (min.)	ml of hypo (N/430)	$[NBS]^{*} \times 10^{4} M$	$(\frac{-dc}{dt}) \times 10^{7}$ $M\ l^{-1}\ s^{-1}$
00	8.56		
05	7.62		
10	7.46		
20	6.82	19.00	5.68
30	6.36		
40	6.00		
60	5.38		
80	4.62		
100	4.08		

TABLE 6.13

$[NBS] = 20.80x10^{-4}M,$ $[Valine] = 4.00x10^{-2}M$

$[HCl] = 4.00x10^{-2}M,$ $[Ir(III)] = 0.60x10^{-6}M$

$[KCl] = 1.00x10^{-3}M,$ $[Hg(OAc)_2] = 3.34x10^{-3}M$

Temperature 30°C

Time (min.)	ml of hypo (M/460)	$[NBS]^* x10^4 M$	$(\frac{-dc}{dt})x10^7$ $M\ l^{-1}\ s^{-1}$
00	9.20		
20	8.92		
40	8.48		
80	7.84	19.20	0.56
160	6.70		
280	5.48		
360	5.02		
420	4.68		
500	3.82		

TABLE 6.14

$[NBS] = 20.00\times10^{-4}$ M, $[Valine] = 4.00\times10^{-2}$ M

$[HCl] = 4.00\times10^{-2}$ M, $[Ir(III)] = 1.20\times10^{-2}$ M

$[KCl] = 1.00\times10^{-2}$ M, $[Hg(OAc)_2] = 3.34\times10^{-3}$ M

Temperature 30°C

Time (min.)	ml of hypo (N/460)	$[NBS]^* \times10^4$	$\left(\frac{-dc}{dt}\right)\times10^7$ M l^{-1} s^{-1}
00	9.20		
10	8.94		
20	8.50		
40	7.82		
80	6.72	19.20	1.08
140	5.52		
180	5.04		
220	4.62		
260	3.80		

TABLE 6.35

$[NBS] = 20 \times 10^{-4} M,$ $[Valine] = 4.00 \times 10^{-2} M$

$[HCl] = 4.00 \times 10^{-2} M,$ $[Ir(III)] = 1.80 \times 10^{-6} M$

$[KCl] = 1.00 \times 10^{-2} M,$ $[Hg(OAc)_2] = 3.34 \times 10^{-3} M$

Temperature $30^{\circ}C$

Time (min.)	ml of hypo (M/460)	$[NBS]^{*} \times 10^{4} M$	$(\frac{-dc}{dt}) \times 10^{7}$ $M\ l^{-1}\ s^{-1}$
00	9.20		
10	8.72		
20	8.22		
30	7.86		
40	7.56	19.20	1.52
60	7.02		
80	6.26		
110	5.68		
140	5.00		
180	4.62		

TABLE 6.16

[NBS] = 20.00×10^{-4} M, [Valine] = 4.00×10^{-2} M

[HCl] = 4.00×10^{-2} M, [Ir(III)] = 2.40×10^{-6} M

[KCl] = 1.00×10^{-2} M, [Hg(OAc)$_2$] = 3.34×10^{-3} M

Temperature 30°C

Time (min.)	ml of hypo (M/460)	$[NBS]^{*} \times 10^{4}$ M	$\left(\frac{-dc}{dt}\right) \times 10^{7}$ M l^{-1} s^{-1}
00	9.20		
10	8.60		
20	8.02		
30	7.52		
40	7.36	19.20	2.14
60	6.66		
80	6.04		
110	5.38		
140	4.78		
180	4.32		

TABLE 6.17

$[NBS] = 20.00 \times 10^{-4}$ M, $[Valine] = 4.00 \times 10^{-2}$ M

$[HCl] = 4.00 \times 10^{-2}$ M, $[Ir(III)] = 3.60 \times 10^{-6}$ M

$[KCl] = 1.00 \times 10^{-2}$ M, $[Hg(OAc)_2] = 3.34 \times 10^{-3}$ M

Temperature 30°C

Time (min.)	ml of hypo (M/460)	$[NBS]^* \times 10^4$ M	$(\frac{-dc}{dt}) \times 10^7$ M l^{-1} s^{-1}
00	9.20		
05	8.74		
10	8.24		
20	7.54		
30	7.04	$\cong$ 19.20	3.08
40	6.24		
60	5.60		
80	4.82		
100	4.20		
120	3.68		

TABLE 6.18

$[NBS] = 20.00 \times 10^{-4} M$, $[Valine] = 4.00 \times 10^{-2} M$

$[HCl] = 4.00 \times 10^{-2} M$, $[Ir(III)] = 5.40 \times 10^{-6} M$

$[KCl] = 1.00 \times 10^{-2} M$, $[Hg(OAc)_2] = 3.34 \times 10^{-3} M$

Temperature $30^{o}C$

Time (min.)	ml of hypo (M/460)	$[NBS]^{*} \times 10^{4} M$	$(\frac{-dc}{dt}) \times 10^{7}$ $M\ l^{-1}\ s^{-1}$
00	9.20		
05	8.62		
10	8.08		
20	7.34		
30	6.82	19.20	4.60
40	6.02		
50	5.62		
60	5.28		
80	4.62		
100	4.06		

The kinetic results reported in tables 6.1 - 6.6, 6.7 - 6.12 and 6.13 - 6.18 have been summarised in tables 6.19, 6.20 and 6.21.

TABLE 6.19

$[NBS] = 20.00 \times 10^{-4}$ M, $[Glycine] = 4.00 \times 10^{-2}$ M

$[HCl] = 4.00 \times 10^{-2}$ M, $[KCl] = 1.00 \times 10^{-2}$ M

$[Hg(OAc)_2] = 3.34 \times 10^{-3}$ M, Temperature 30°C

$[Ir(III)] \times 10^{6}$ M	$\left(\frac{-dc}{dt}\right) \times 10^{7}$ M l^{-1} s^{-1}	$10^{4} k_1 = \frac{(-dc/dt)}{[NBS]^{*}}$ s^{-1}	$10^{-1} k_2 = \frac{k_1}{[Ir(III)]}$ $M^{-1} L s^{-1}$
0.60	1.08	0.59	9.83
1.20	2.10	1.14	9.50
1.80	3.32	1.80	10.00
2.40	4.14	2.25	9.38
3.60	6.58	3.57	9.92
5.40	9.82	5.34	9.89

$[NBS]^{*} = 18.40 \times 10^{-4}$ M at which $\left(\frac{-dc}{dt}\right)$ was determined

TABLE 6.20

$[NBS] = 20.00 \times 10^{-4} M$, $[Alanine] = 4.00 \times 10^{-2} M$

$[HCl] = 10.00 \times 10^{-2} M$, $[KCl] = 1.00 \times 10^{-2} M$

$[Hg(OAc)_2] = 3.34 \times 10^{-3} M$, Temperature $30^{\circ}C$

$[Ir(III)] \times 10^6 M$	$(\frac{-dc}{dt}) \times 10^7$ $M\ l^{-1}\ s^{-1}$	$10^4 k_1 = \frac{(-dc/dt)}{[NBS]^*}$ s^{-1}	$10^{-1} k_2 = \frac{k_1}{[Ir(III)]}$ $M^{-1} L s^{-1}$
0.60	0.65	0.34	5.66
1.20	1.26	0.66	5.55
1.80	1.94	1.02	5.66
2.40	2.56	1.35	5.62
3.60	3.82	2.01	5.60
5.40	5.68	2.99	5.54

$[NBS]^* = 19.00 \times 10^{-4} M$ at which $(-dc/dt)$ was determined

TABLE 6.21

$[NBS] = 20.00 \times 10^{-4}$ M, $[Valine] = 4.00 \times 10^{-2}$ M

$[HCl] = 4.00 \times 10^{-2}$ M, $[KCl] = 1.00 \times 10^{-2}$ M

$[Hg(OAc)_2] = 3.34 \times 10^{-3}$ M, Temperature 30°C

$[Ir(III)] \times 10^6$ M	$(-dc/dt) \times 10^7$ M l^{-1} s^{-1}	$10^4 k_1 = \frac{(-dc/dt)}{[NBS]^*}$ sec^{-1}	$10^{-1} k_2 = \frac{k_1}{[Ir(III)]}$ $M^{-1} L s^{-1}$
0.60	0.56	0.29	4.83
1.20	1.08	0.56	4.67
1.80	1.52	0.79	4.28
2.40	2.14	1.11	4.66
3.60	3.06	1.59	4.42
5.40	4.60	2.40	4.44

$[NBS]^* = 19.20 \times 10^{-4}$ M at which $(\frac{-dc}{dt})$ was determined

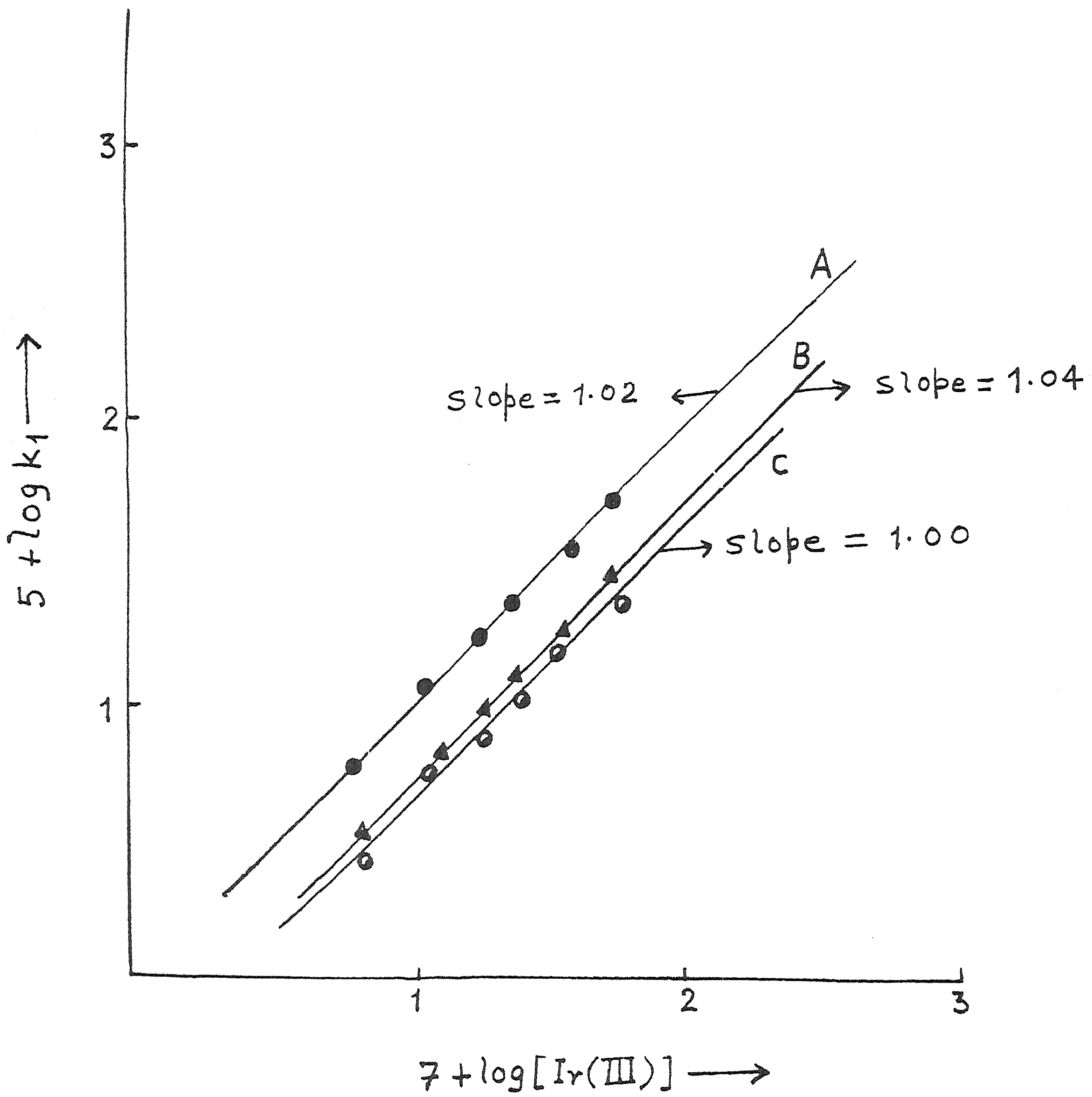

FIG. 6.1 : A → Under the conditions of Table 6.19 (GLYCINE)

B → Under the conditions of Table 6.20 (ALANINE)

C → Under the conditions of Table 6.21 (VALINE)

It is evident from the data of tables 6.19, 6.20 and 6.21 that on increasing the concentration of Ir(III) the value of k_1 increases in direct proportionality which shows that order of the reaction with respect to Ir(III) is one in oxidation of each amino acids used here. The constant values of k_2 also confirm first order in Ir(III).

When log k_1 values are plotted against log [Ir(III)], a straight line with (Fig. 6.1) slope nearly one is obtained. This shows that all reactions follow first -order kinetics in Iridium(III) chl-oride in oxidation of all amino acids used here. The constant k_2 values of tables 6.19, 6.20 and 6.21 confirm that order with respect to Ir(III) is one.

CHAPTER VII

DETERMINATION OF DEPENDENCE OF REACTIONS ON CHLORIDE IONS IN NBS-AMINO ACIDS REDOX SYSTEMS WITH Ir(III) AS CATALYST

7 : DETERMINATION OF DEPENDENCE OF REACTION ON CHLORIDE ION CONCENTRATION IN NBS-AMINO ACID REDOX SYSTEM

In this chapter an attempt has been made to determine the effect of addition of chloride ions on the rate constant of Ir(III) chloride catalysed oxidation of glycine, alanine and valine by acidic solution of N-bromosuccinimide. For this purpose in this chapter potassium chloride has been used as source of chloride ions. In order to obtain the above aim, various experiments have been performed at different concentrations of potassium chloride but at fixed concentrations of all other reactants. It has been observed that reactions are not influenced by changing the concentrations of potassium chloride. This show zero effect of addition of chloride ions on reaction between NBS and each of amino acids. The kinetic results reported in tables 7.1, 7.2 and 7.3 in summarised form clearly show negligible effect of added chloride ions on the reaction rate.

TABLE 7.1

[NBS] = 10.00×10^{-4} M, [Glycine] = 2.00×10^{-2} M

[HCl] = 4.00×10^{-2} M, [Ir(III)] = 4.80×10^{-6} M

[Hg(OAc)$_2$] = 3.34×10^{-3} M, Temperature 30°C

[KCl] $\times 10^2$ M	$k_1 \times 10^4$ sec^{-1}
1.00	4.33
1.50	4.28
2.00	4.30
2.50	4.32
3.00	4.29
3.50	4.31
4.00	4.28

TABLE 7.2

$[NBS] = 10.00 \times 10^{-4}$ M, $[Alanine] = 2.00 \times 10^{-2}$ M

$[HCl] = 10.00 \times 10^{-2}$ M, $[Ir(III)] = 4.80 \times 10^{-6}$ M

$[Hg(OAc)_2] = 3.34 \times 10^{-3}$ M, Temperature 30°C

$[KCl] \times 10^2$ M	$k_1 \times 10^4$ sec^{-1}
1.00	1.53
1.50	1.56
2.00	1.54
3.00	1.50
4.00	1.54
5.00	1.55
6.00	1.49
7.50	1.53

TABLE 7.3

[NBS] = 10.00×10^{-4} M, [Valine] = 2.00×10^{-2} M

[HCl] = 4.00×10^{-2} M, [Ir_x(III)] = 4.80×10^{-6} M

[$Hg(OAc)_2$] = 3.34×10^{-3} M, Temperature 30°C

[KCl] $\times 10^2$ M	$k_1 \times 10^4$ sec^{-1}
1.00	1.22
2.00	1.20
3.00	1.26
4.00	1.23
5.00	1.24
6.00	1.23
7.50	1.24

CHAPTER VIII

DETERMINATION OF DEPENDENCE OF REACTIONS OF MERCURIC ACETATE IN NBS - AMINO ACIDS REDOX SYSTEM WITH I_2 (III) AS CATALYST

8 : DETERMINATION OF EFFECT OF VARIATION OF CONCENTRATION OF MERCURIC ACETATE ON RATE OF OXIDATION OF AMINO ACIDS BY ACIDIC SOLUTION OF N-BROMO - SUCCINIMIDE

In the present thesis mercuric acetate has been used as scavenger for bromide ions as bromide ions (reaction product) on interaction with NBS produced Br_2 which complicated the reaction by setting another parallel oxidations. Mercuric acetate can also function as oxidant and catalyst. Hence in order to prove whether it acts in the present case as oxidant or not, some experiments were carried out with mercuric acetate without adding NBS in the reaction mixture and it was observed that reactions did not proceed. Hence possibility of its action as oxidant is ruled out. Now here in the present chapter an attempt is being made to see whether it is involved as catalyst or not. The results of experiments performed at different concentrations of mercuric acetate are recorded in tables 8.1, 8.2 and 8.3 which indicate negligible effect of mercuric acetate proving that it is not involved as homogeneous catalyst.

TABLE 8.1

[NBS] = 10.00×10^{-4} M, [HCl] = 4.00×10^{-2} M

[KCl] = 2.00×10^{-2} M, [Ir(III)] = 4.80×10^{-6} M

[Glycine] = 1.00×10^{-2} M, Temperature $30^{\circ}C$

[$Hg(OAc)_2$] $\times 10^{3}$ M	$k_1 \times 10^{4}$ sec^{-1}
1.25	2.24
1.50	2.26
1.75	2.28
2.00	2.27
2.50	2.22
3.00	2.24
3.34	2.22
3.50	2.26

TABLE 8.2

[NBS] = 10.00×10^{-4} M, [HCl] = 10.00×10^{-2} M

[KCl] = 2.50×10^{-2} M, [I_r (III)] = 4.80×10^{-6} M

[Alanine] = 4.00×10^{-2} M, Temperature $30^{\circ}C$

$[Hg(OAc)_2]\times10^3$ M	$k_1\times10^4$ sec^{-1}
1.25	2.95
1.50	2.91
2.00	2.93
2.50	2.92
3.00	2.94
3.34	2.95
3.75	2.98
4.00	2.93

TABLE 8.3

[NBS] = 10.00×10^{-4} M, [HCl] = 4.00×10^{-2} M

[KCl] = 2.00×10^{-2} M, [Ir(III)] = 4.80×10^{-6} M

[Valine] = 2.00×10^{-2} M, Temperature 30°C

[$Hg(OAc)_2$] $\times 10^3$ M	$k_1 \times 10^4$ sec^{-1}
1.25	1.22
1.50	1.20
2.00	1.23
2.50	1.24
3.00	1.19
3.50	1.25
4.00	1.24
5.00	1.22

CHAPTER IX

DETERMINATION OF EFFECT OF VARIATION OF IONIC STRENGTH OF MEDIUM ON RATE CONSTANTS OF OXIDATION OF AMINO ACIDS BY ACIDIC NBS SOLUTIONS WITH Ir(III) AS CATALYST

DETERMINATION OF EFFECT OF VARIATION OF IONIC STRENGTH OF THE MEDIUM ON RATE OF OXIDATION OF AMINO ACIDS BY ACETIC SOLUTION OF N-BROMOSUCCINIMIDE

Ionic strength of the medium plays an important role in the field of study of reaction mechanism. It helps to detect the nature of reactive species i.e. whether the reactive species are similarly charged or dissimilarly charged or one of them is neutral. Thus nature of reacting species involved in the rate determining step is determined by means of kinetic studies. In order to obtain the above aim, a few experiments with different ionic strengths of the medium have been conducted at constant concentrations of all other reactants and results of these experiments have been summarised in tables 9.1, 9.2 and 9.3 in oxidation of glycine, alanine and valine respectively. These results clearly indicate negligible effect of variation of ionic strength of the medium on the reaction rate of the title reactions. Ionic strength of the medium has been varied by the addition of suitable amounts of sodium perchlorate.

TABLE 9.2

$[NBS] = 10.00\times10^{-4}M$, $[HCl] = 10.00\times10^{-2}M$

$[Alanine] = 1.00\times10^{-2}M$, $[KCl] = 4.00\times10^{-2}M$

$[Ir(III)] = 4.80\times10^{-6}M$, $[Hg(OAc)_2] = 3.34\times10^{-3}M$

$[NaClO_4]\times10^4 M$	Ionic strength $(\mu)\times10M$	$k_1 \times 10^4$ sec^{-1}
0.90	2.40	0.78
1.00	3.40	0.79
2.00	4.40	0.80
3.00	5.40	0.77
4.00	6.40	0.79
5.00	7.40	0.78
7.50	9.90	0.79

TABLE 9.3

[NBS] = 10.00×10^{-4} M, [HCl] = 4.00×10^{-2} M

[Valine] = 2.50×10^{-2} M, [KCl] = 2.00×10^{-2} M

[$Ir(III)$] = 4.80×10^{-6} M, [$Hg(OAc)_2$] = 3.34×10^{-3} M

[$NaClO_4$] x 10 M	[Ionic strength (μ) x10M	k_1 $\times 10^4$ M sec^{-1}
0.90	1.60	1.39
1.00	2.60	1.38
2.00	3.60	1.38
3.00	4.60	1.37
4.00	5.60	1.40
5.00	6.60	1.38
7.50	9.10	1.37

CHAPTER X

DETERMINATION OF EFFECT OF VARIATION OF SUCCINIMIDE CONCENTRATION ON RATE OF OXIDATION OF AMINO ACIDS BY ACIDIC SOLUTION OF N-BROMOSUCCINIMIDE WITH Ir(III) AS CATALYST

10 : DETERMINATION OF EFFECT OF VARIATION OF CONCEN - TRATION OF SUCCINIMIDE ON THE RATE OF OXIDATION OF AMINO ACIDS BY ACIDIC SOLUTION OF N -BROMO - SUCCINIMIDE

Succinimide is one of products of the title reaction. Hence it is essential to study its effect on the rate of the amino acids by NBS. Hence in order to realise the above aim, a larger number of experiments with different concentrations of succinimide and at constant concentrations of all other reactants were done the results of various experiments obtained in oxidation of glycine, alanine and valine have been recorded in tables 10.1 - 10.5, 10.6 - 10.10 and 10.11 - 10.15 respectively. It is clear from the data of aforesaid tables that increase in concentration of succinimide in the reaction mixture greatly influence the first - order rate constant obtained in oxidation of aforesaid amino acids by acidic solution of N-bromosuccinimide. Succinimide effect also helps in deciding the reactive species of N-bromosuccinimide in acidic media.

TABLE 10.1

$[NBS] = 10.00 \times 10^{-4} M$, $[Glycine] = 2.00 \times 10^{-2} M$

$[HCl] = 4.00 \times 10^{-2} M$, $[Ir(III)] = 4.80 \times 10^{-6} M$

$[KCl] = 2.00 \times 10^{-2} M$, $[Hg(OAc)_2] = 3.34 \times 10^{-3} M$

Succinimide $= 1.25 \times 10^{-3} M$ Temperature

Time (min.)	ml of hypo (N/812)	$[NBS]^{*} \times 10^{4} M$	$\left(\frac{-dc}{dt}\right) \times 10^{7}$ $M\ l^{-1}\ s^{-1}$
00	8.12		
05	6.82		
10	6.30		
20	5.26	9.00	2.52
30	4.58		
40	4.26		
60	3.86		
80	3.42		
100	3.04		

TABLE 10.2

$[NBS] = 10.00 \times 10^{-4} M.$ $[Glycine] = 2.00 \times 10^{-2} M$

$[HCl] = 4.00 \times 10^{-2} M.$ $[Ir(III)] = 4.80 \times 10^{-6} M$

$[KCl] = 2.00 \times 10^{-2} M.$ $[Hg(OAc)_2] = 3.34 \times 10^{-3} M$

$[Succinimide] = 1.43 \times 10^{-3} M.$ Temperature $30^{\circ}C$

Time (min.)	ml of hypo (N/812)	$[NBS]^{*} \times 10^{4} M$	$k_1 \times 10^{4}$ sec^{-1}
00	8.12		
05	7.30		
10	6.64		
20	5.86	9.00	2.30
30	5.56		
50	4.66		
70	4.20		
100	3.64		
130	3.40		

TABLE 10.3

[NBS] = 10.00x10^{-4}M, [Glycine] = 2.00x10^{-2}M

[HCl] = 4.00x10^{-2} M, [I_r(III)] = 4.80x10^{-6}M

[KCl] = 2.00x10^{-2} M, [Hg(OAc)$_2$] = 3.34x10^{-3}M

[Succinimide] = 1.67x10^{-3}M, Temperature 30°C

Time (min.)	ml of hypo (N/812)	[NBS]*x10^4M	($\frac{-dc}{dt}$)x10^7 M l^{-1} s^{-1}
00	8.12		
05	9.42		
10	6.92		
20	6.28		
30	5.74	9.00	2.06
50	4.90		
70	4.36		
100	3.76		
130	3.60		

TABLE 10.4

$[NBS] = 10.00 \times 10^{-4}$ M, $[Glycine] = 2.00 \times 10^{-2}$ M

$[HCl] = 4.00 \times 10^{-2}$ M, $[Ir(III)] = 4.80 \times 10^{-6}$ M

$[KCl] = 2.00 \times 10^{-2}$ M, $[Hg(OAc)_2] = 3.34 \times 10^{-3}$ M

$[succinimide] = 2.00 \times 10^{-3}$ M, Temperature $30^{\circ}C$

Time (min.)	ml of hypo (N/812)	$[NBS]^{*} \times 10^{4}$ M	$(\frac{-dc}{dt}) \times 10^{7}$ M l^{-1} s^{-1}
00	8.12		
05	7.42		
10	6.94		
20	6.10	9.00	1.90
40	5.08		
60	4.38		
90	3.92		
120	3.16		
180	2.82		

TABLE 10.5

$[NBS] = 10.00 \times 10^{-4} M$, $[Glycine] = 2.00 \times 10^{-2} M$

$[HCl] = 4.00 \times 10^{-2} M$, $[Ir(III)] = 4.00 \times 10^{-6} M$

$[KCl] = 2.00 \times 10^{-2} M$, $[Hg(OAc)_2] = 3.34 \times 10^{-3} M$

$[Succinimide] = 2.50 \times 10^{-3} M$, Temperature $30^{o}C$

Time (min.)	ml of hypo (N/812)	$[NBS]^{*} \times 10^{4} M$	$\left(\frac{-dc}{dt}\right) \times 10^{7}$ $M\ l^{-1}\ s^{-1}$
00	8.12		
05	7.54		
10	7.02		
20	6.28		
40	5.52	9.00	1.56
60	4.86		
80	4.52		
120	3.64		
180	3.34		

TABLE 10.6

$[NBS] = 10.00 \times 10^{-4}$ M, $[Alanine] = 2.00 \times 10^{-2}$ M

$[HCl] = 10.00 \times 10^{-2}$ M, $[I_r(III)] = 4.80 \times 10^{-6}$ M

$[KCl] = 2.00 \times 10^{-2}$ M $[Hg(OAc)_2] = 3.34 \times 10^{-3}$ M

$[Succinimide] = 1.43 \times 10^{-3}$, Temperature 30°C

Time (min.)	ml of hypo (N/884)	$[NBS]^* \times 10^4$ M	$(\frac{-dc}{dt}) \times 10^7$ M l^{-1} s^{-1}
00	8.84		
05	8.06		
10	7.62		
20	6.64	9.00	1.94
40	5.56		
70	4.54		
110	3.64		
160	3.20		
220	2.76		

TABLE 10.7

[NBS] = 10.00×10^{-4} M, [Alanine] = 2.00×10^{-2} M

[HCl] = 10.00×10^{-2} M, [Ir(III)] = 4.80×10^{-6} M

[KCl] = 2.00×10^{-2} M, [Hg(OAc)$_2$] = 3.34×10^{-3} M

[Succinimide] = 1.67×10^{-3} M, Temperature 30°C

Time (min.)	m l of hypo (N/800)	$[NBS]^{*} \times 10^{4}$ M	$(\frac{-dc}{dt}) \times 10^{7}$ M l^{-1} s^{-1}
00	8.84		
05	8.22		
10	7.68		
20	7.06		
~~9.00~~	~~1.64~~		
40	6.04	9.00	1.64
70	4.96		
110	4.08		
160	3.66		
220	3.40		

TABLE 10.[illegible]

[NBS] = 10.00×10^{-4} M, [Alanine] = 2.00×10^{-2} M

[HCl] = 10.00×10^{-2} M, [Ir(III)] = 4.80×10^{-6} M

[KCl] = 2.00×10^{-2} M, [$Hg(OAc)_2$] = 3.34×10^{-3} M

[Succinimide] = 1.00×10^{-3} M, Temperature 30°C

Time (min.)	ml of hypo (M/884)	$[NBS]^{*}\times10^{4}$ M	$\left(\frac{-dc}{dt}\right)\times10^{7}$ M $l^{-1}s^{-1}$
00	8.84		
05	8.48		
10	8.06		
20	7.08		
40	5.76	9.00	1.34
70	4.88		
110	3.98		
160	3.64		
220	3.52		

TABLE 10.9

$[NBS] = 10.00\times10^{-4}$ M, $[Alanine] = 2.00\times10^{-2}$ M

$[HCl] = 10.00\times10^{-2}$ M, $[I_r(III)] = 4.80\times10^{-6}$ M

$[KCl] = 2.00\times10^{-2}$ M, $[Hg(OAc)_2] = 3.34\times10^{-3}$ M

$[Succinimide] = 2.50\times10^{-3}$, Temperature 30°C

Time (min.)	ml of hypo (M/884)	$[NBS]^{*}\times10^{4}$	$(\frac{-dc}{dt})\times10^{7}$ $M\ l^{-1}\ s^{-1}$
00	8.84		
05	8.66		
10	8.30		
20	8.04	9.00	0.96
40	6.88		
70	5.76		
110	4.50		
160	3.82		
220	3.16		

TABLE 10.10

[NBS] = 10.00×10^{-4} M, [Alanine] = 2.00×10^{-2} M

[HCl] = 10.00×10^{-2} M, [I_r(III)] = 4.80×10^{-6} M

[KCl] = 2.00×10^{-2} M, [Hg(OAc)$_2$] = 3.34×10^{-3} M

[succinimide] = 3.33×10^{-3} M, Temperature 30°C

Time (min.)	ml of hypo (N/884)	[NBS]$^* \times 10^4$ M	$(\frac{-dc}{dt}) \times 10^7$ M $l^{-1} s^{-1}$
00	8.84		
05	8.56		
10	8.38		
20	8.12	9.00	0.75
40	7.16		
70	5.94		
110	4.96		
160	4.06		
220	3.32		

TABLE 10.11

[NBS] = 10.00×10^{-4} M, [Valine] = 2.00×10^{-2} M

[HCl] = 4.00×10^{-2} M, [Ir(III)] = 4.80×10^{-6} M

[KCl] = 2.00×10^{-2} M, [$Hg(OAc)_2$] = 3.34×10^{-3} M

[Succinimide] = 1.43×10^{-3} M, Temperature 30°C

Time (min.)	ml of hypo (N/896)	$[NBS]^{*} \times 10^{4}$ M	$\left(\frac{-dc}{dt}\right) \times 10^{7}$ $M\ l^{-1} s^{-1}$
00	8.56		
05	8.32		
10	8.22		
20	7.70		
40	6.96	9.00	0.94
80	5.76		
140	5.02		
200	4.26		
260	3.44		

TABLE 10.12

[NBS] = 10.00×10^{-4} M, [Valine] = 2.00×10^{-2} M

[HCl] = 4.00×10^{-2} M, [Ir(III)] = 4.80×10^{-6} M

[KCl] = 2.00×10^{-2} M, [Hg(OAc)$_2$] = 3.34×10^{-3} M

[Succinimide] = 1.67×10^{-3} M, Temperature 30°C

Time (min.)	ml of hypo (N/856)	[NBS]$^* \times 10^4$ M	$\left(\frac{-dc}{dt}\right) \times 10^7$ M l^{-1} s^{-1}
00	8.56		
05	8.38		
10	8.16		
20	7.88	9.00	0.84
40	7.04		
80	5.74		
140	4.56		
200	3.84		
260	3.38		

TABLE 10.13

[NBS] = 10.00×10^{-4} M, [Valine] = 2.00×10^{-2} M

[HCl] = 4.00×10^{-2} M, [I_2 (III)] = 4.80×10^{-6} M

[KCl] = 2.00×10^{-2} M, [Hg $(OAc)_2$] = 3.34×10^{-3} M

[Succinimide] = 2.00×10^{-3} M, Temperature 30°C

Time (min.)	ml of hypo (N/856)	$[NBS]^* \times 10^4$ M	$(\frac{-dc}{dt}) \times 10^7$ M l^{-1} s^{-1}
00	8.56		
05	8.30		
10	8.12		
20	7.84		
40	7.12	9.00	0.72
80	5.96		
140	4.58		
200	3.74		
260	3.54		

TABLE 10.14

[NBS] = 10.00×10^{-4} M, [Valine] = 2.00×10^{-2} M

[HCl] = 4.00×10^{-2} M, [Ir(III)] = 4.80×10^{-6} M

[KCl] = 2.00×10^{-2} M, [Hg(OAc)$_2$] = 3.34×10^{-3} M

[Succinimide] = 2.50×10^{-3} M, Temperature 30°C

Time (min.)	ml of hypo (N/856)	[NBS]$^* \times 10^4$ M	$(\frac{-dc}{dt}) \times 10^7$ M l^{-1} s^{-1}
00	8.56		
05	8.36		
10	8.12		
20	7.80		
40	7.30	9.00	0.64
80	6.34		
140	4.92		
200	4.06		
260	3.72		

TABLE 10.15

[NBS] = 10.00×10^{-4} M, [Valine] = 2.00×10^{-2} M

[HCl] = 4.00×10^{-2} M, [I_r(III)] = 4.80×10^{-6} M

[KCl] = 2.00×10^{-2} M, [$Hg(OAc)_2$] = 3.34×10^{-3} M

[Succinimide] = 3.33×10^{-3} M, Temperature 30°C

Time (min.)	ml of hypo (N/856)	$[NBS]^* \times 10^4$ M	$(\frac{-dc}{dt}) \times 10^7$ M l^{-1} s^{-1}
00	8.56		
05	8.40		
10	8.18		
20	7.84	9.00	0.54
40	7.20		
80	6.16		
140	5.02		
200	4.06		
260	3.62		

The results recorded in tables 10.1 - 10.5, 10.6-10.10 and 10.11 - 10.15 in oxidation of glycine, alanine and valine at various concentrations of Succinimide have been summarised in tables 10.16, 10.17 and 10.18 respectively.

TABLE 10.16

[NBS] = 10.00×10^{-4} M, [Glycine] = 2.00×10^{-2} M

[KCl] = 2.00×10^{-2} M, [Ir(III)] = 4.80×10^{-6} M

[HCl] = 4.00×10^{-2} M, [Hg(OAc)$_2$] = 3.34×10^{-3} M

Temperature 30°C

[Succinimide] x 10^3 M	$(\frac{-dc}{dt})\times10^7$ M l^{-1} s^{-1}	$k_1 \times 10^4$ sec^{-1}
1.25	2.52	2.80
1.43	2.30	2.55
1.67	2.06	2.30
2.00	1.90	2.11
2.50	1.56	1.73

[NBS]* = 9.00×10^{-4} M at which $(-dc/dt)$ was determined

TABLE 10.17

$[NBS] = 10.00 \times 10^{-4}$ M, $[Glycine] = 2.00 \times 10^{-2}$ M

$[KCl] = 2.00 \times 10^{-2}$ M, $[Ir(III)] = 4.80 \times 10^{-6}$ M

$[HCl] = 8.00 \times 10^{-2}$ M, $[Hg(OAc)_2] = 3.34 \times 10^{-3}$ M

Temperature 30°C

[Succinimide] $\times 10^3$ M	$\left(\frac{-dc}{dt}\right) \times 10^7$ M l^{-1} s^{-1}	$k_1 \times 10^4$ sec^{-1}
1.43	1.94	2.15
1.67	1.64	1.82
2.00	1.34	1.50
2.50	0.96	1.06
3.33	0.75	0.83

$[NBS]^* = 9.00 \times 10^{-4}$ M at which $\left(\frac{-dc}{dt}\right)$ was determined

TABLE 10.18

[NBS] = 10.00×10^{-4} M,   [Valine] = 2.00×10^{-2} M

[HCl] = 4.00×10^{-2} M,   [I_2 (III)] = 4.80×10^{-6} M

[KCl] = 2.00×10^{-2} M,   [$Hg(OAc)_2$] = 3.34×10^{-3} M

Temperature 30°C

[Succinimide] $\times 10^3$ M,	$(\frac{-dc}{dt}) \times 10^7$ $M\ l^{-1}\ s^{-1}$	$k_1 \times 10^4$ sec^{-1}
1.43	0.94	1.04
1.67	0.84	0.93
2.00	0.72	0.80
2.50	0.64	0.70
3.33	0.54	0.60

[NBS]* = 9.00×10^{4} M at which $(\frac{-dc}{dt})$ was determined

It is evident from the data of summarised tables 10.16 - 10.18 that on increasing [Succinimide] the value of k_1 decreases showing negative effect of succinimide on the rate of reaction.

CHAPTER XI

STUDY OF EFFECT OF VARIATION OF TEMPERATURE ON THE RATE OF OXIDATION OF AMINO ACIDS BY NBS WITH ACIDIC SOLUTION OF Ir(III) CHLORIDE

11. STUDY OF EFFECT OF VARIATION OF TEMPERATURE ON THE RATE OF OXIDATION OF AMINO ACIDS BY N-BROMOSUCCINIMIDE IN ACIDIC MEDIA

The redox systems involving N-bromosuccinimide and amino acids viz. glycine, alanine and valine as oxidant and reductants respectively have been studied in the presence of iridium (III) chloride as homogeneous catalyst at 30°C in details. These reactions have been studied at 35, 40 and 45°C. The results of such experiments have been recorded in tables 11.1 - 11.3, 11.4 - 11.6 and 11.7 - 11.9 in oxidation of glycine, alanine and valine respectively. It is clear from the data of results of tables 11.1 - 11.9 that on increasing the temperature the reaction rate is significantly increased.

TABLE 11.1

$NBS = 10.00 \times 10^{-4} M$, Glycine $= 2.00 \times 10^{-2} M$

$KCl = 4.00 \times 10^{-2} M$, $Ir(III) = 4.80 \times 10^{-6} M$

$HCl = 1.00 \times 10^{-2} M$, $Hg(OAc)_2 = 3.34 \times 10^{-3} M$

Temperature 35°C

Time (min.)	ml of hypo (N/920)	$NBS^{*} \times 10^{4} M$	$(\frac{-dc}{dt}) \times 10^{7}$ $M\,l^{-1}s^{-1}$
00	9.28		
05	7.82		
10	6.72		
20	5.14	9.00	4.58
30	4.06		
40	3.62		
50	3.24		
60	3.20		
70	3.06		

TABLE 11.2

$NBS = 10.00 \times 10^{-4} M$, Glycine $= 2.00 \times 10^{-2} M$

$HCl = 4.00 \times 10^{-2} M$, $Ir(III) = 4.80 \times 10^{-6} M$

$KCl = 1.00 \times 10^{-2} M$, $Hg(OAc)_2 = 3.34 \times 10^{-3} M$

Temperature $40^{\circ}C$

Time (min.)	ml of hypo (N/920)	$NBS^{*} \times 10^{4} M$	$\left(\frac{-dc}{dt}\right) \times 10^{7}$ $M\ l^{-1} s^{-1}$
00	9.28		
05	7.48		
10	6.18		
20	4.36		
30	3.72	9.00	7.50
40	3.28		
50	3.08		
60	2.92		
70	2.86		

TABLE 11.3

NBS = 10.00×10^{-4} M, Glycine = 2.00×10^{-2} M

HCl = 4.00×10^{-2} M, Ir(III) = 4.80×10^{-6} M

KCl = 1.00×10^{-2} M, $Hg(OAc)_2$ = 3.34×10^{-3} M

Temperature 45°C

Time (min.)	ml of hypo (N/928)	$NBS^{*}\times10^{4}$ M	$(-\frac{dc}{dt})\times10^{7}$ $M\ l^{-1}\ s^{-1}$
00	9.28		
05	7.18		
10	5.56		
20	3.86		
30	3.16	9.00	13.33
40	2.96		
50	2.80		
60	2.76		
70	2.64		

TABLE 11.4

NBS = 10.00×10^{-4} M, Alanine = 2.00×10^{-2} M

HCl = 10.00×10^{-2} M, Ir(III) = 4.80×10^{-6} M

KCl = 1.00×10^{-2} M, $Hg(OAc)_2$ = 3.34×10^{-3} M

Temperature $35^{\circ}C$

Time (min.)	ml of hypo (N/840)	NBS* $\times 10^{4}$ M	$\left(\frac{-dc}{dt}\right) \times 10^{7}$ $Ml^{-1}\ s^{-1}$
00	8.40		
05	7.92		
10	7.60		
20	6.62	9.00	1.65
40	5.04		
60	4.00		
80	3.56		
100	2.96		
120	2.24		

TABLE 11.5

$NBS = 10.00\times10^{-4} M$, $Alanine = 2.00\times10^{-2} M$

$HCl = 10.00\times10^{-2} M$, $Ir(III) = 4.80\times10^{-6} M$

$KCl = 1.00\times10^{-3} M$, $Hg(OAc)_2 = 3.34\times10^{-3} M$

Temperature 80°C

Time (min.)	ml of hypo (N/840)	$NBS^{*} \times10^{4} M$	$\left(\frac{-dc}{dt}\right)\times10^{7}$ $M\ l^{-1} s^{-1}$
00	8.40		
05	7.64		
10	7.10		
20	5.86	9.00	2.50
30	4.82		
40	4.16		
50	3.70		
60	3.32		
70	2.92		

TABLE 11.6

NBS = 10.00×10^{-4} M, Alanine = 2.00×10^{-2} M

HCl = 10.00×10^{-2} M, I_r(III) = 4.00×10^{-6} M

KCl = 1.00×10^{-2} M, Hg(OAc)$_2$ = 3.34×10^{-3} M

Temperature 45°C

Time (min.)	ml of hypo (N/840)	NBS* $\times10^4$ M	$(-\frac{dc}{dt})\times10^7$ M l^{-1} Se^{-1}
00	8.40		
05	7.30		
10	6.42		
15	5.36	9.00	4.40
20	4.70		
25	4.08		
30	3.72		
35	3.52		
45	3.00		

TABLE 11.7

NBS = 10.00×10^{-4} M, Valine = 2.00×10^{-2} M

HCl = 4.00×10^{-2} M, Ir(III) = 4.00×10^{-6} M

KCl = 1.00×10^{-2} M, $Hg(OAc)_2$ = 3.34×10^{-3} M

Temperature 35°C

Time (min.)	ml of hypo (N/1020)	NBS* $\times 10^{4}$ M	$(\frac{-dc}{dt}) \times 10^{7}$ M l^{-1} s^{-1}
00	10.20		
05	9.50		
10	9.06		
20	8.16		
40	6.38	9.00	1.16
60	5.00		
80	4.16		
100	3.54		
120	3.20		

TABLE 11.8

NBS $= 10.00 \times 10^{-4}$ M, Valine $= 2.00 \times 10^{-2}$ M

HCl $= 4.00 \times 10^{-2}$ M, I_r(XIX) $= 4.80 \times 10^{-6}$ M

KCl $= 1.00 \times 10^{-2}$ M, Hg(OAc)$_2$ $= 3.34 \times 10^{-3}$ M

Temperature 40°C

Time (min.)	ml of hypo (N/784)	NBS° $\times 10^4$ M	$\left(\frac{-dc}{dt}\right) \times 10^7$ M l^{-1} s^{-1}
00	10.20		
05	9.18		
10	8.00		
20	6.56		
30	5.30	9.00	2.91
40	4.50		
50	3.72		
60	3.46		
70	3.10		

TABLE 11.9

$HBE = 10.00 \times 10^{-4}$ M, Valine $= 2.00 \times 10^{-2}$ M

$HCl = 4.00 \times 10^{-2}$ M, $Ir(III) = 4.80 \times 10^{-4}$ M

$KCl = 1.00 \times 10^{-2}$ M, $Hg(OAc)_2 = 3.34 \times 10^{-3}$ M

Temperature 45°C

Time (min.)	ml of hypo (N/1000)	$HBE^* \times 10^4$ M	$\left(\frac{-dc}{dt}\right) \times 10^7$ M l^{-1} s^{-1}
00	10.20		
05	7.52		
10	6.40		
15	5.36		
20	4.56	9.00	5.00
25	4.04		
30	3.62		
35	3.30		
40	3.10		

The kinetic results of tables 11.1 - 11.3 and $30^{\circ}C$, tables 11.4 - 11.6 and at $30^{\circ}C$ and tables 11.7 - 11.9 and at $30^{\circ}C$ have been summarised in tables 11.10, 11.11 and 11.12 respectively.

TABLE 11.10

NBS = 10.00×10^{-4} M, Glycine = 2.00×10^{-2} M

HCl = 4.00×10^{-2} M, I_2(III) = 4.80×10^{-4} M

KCl = 1.00×10^{-2} M, $Hg(OAc)_2$ = 3.34×10^{-3} M

Temperature ($^{\circ}C$)	$k_1 \times 10^4$ sec^{-1}
30	2.78
35	5.09
40	8.33
45	14.81

TABLE 11.11

NBS = 10.00×10^{-6} M,

HCl = 10.00×10^{-2} M,

KCl = 1.00×10^{-2} M,

Alanine = 2.00×10^{-2} M,

Ir(III) = 4.00×10^{-6} M,

$Hg(OAc)_2$ = 3.34×10^{-3} M

Temperature ($^{\circ}$C)	$k_1 \times 10^4$ sec^{-1}
30	0.92
35	1.61
40	2.78
45	4.89

TABLE 11.12

$NBS = 10.00 \times 10^{-4}$ M,

$HCl = 4.00 \times 10^{-2}$ M,

$KCl = 1.00 \times 10^{-2}$ M,

$Valine = 2.00 \times 10^{-2}$ M,

$I_r(III) = 4.80 \times 10^{-6}$ M,

$Hg(OAc)_2 = 3.34 \times 10^{-3}$ M

Temperature (^{o}C)	$k_1 \times 10^4$ sec^{-1}
30	1.00
35	1.84
40	3.23
45	5.56

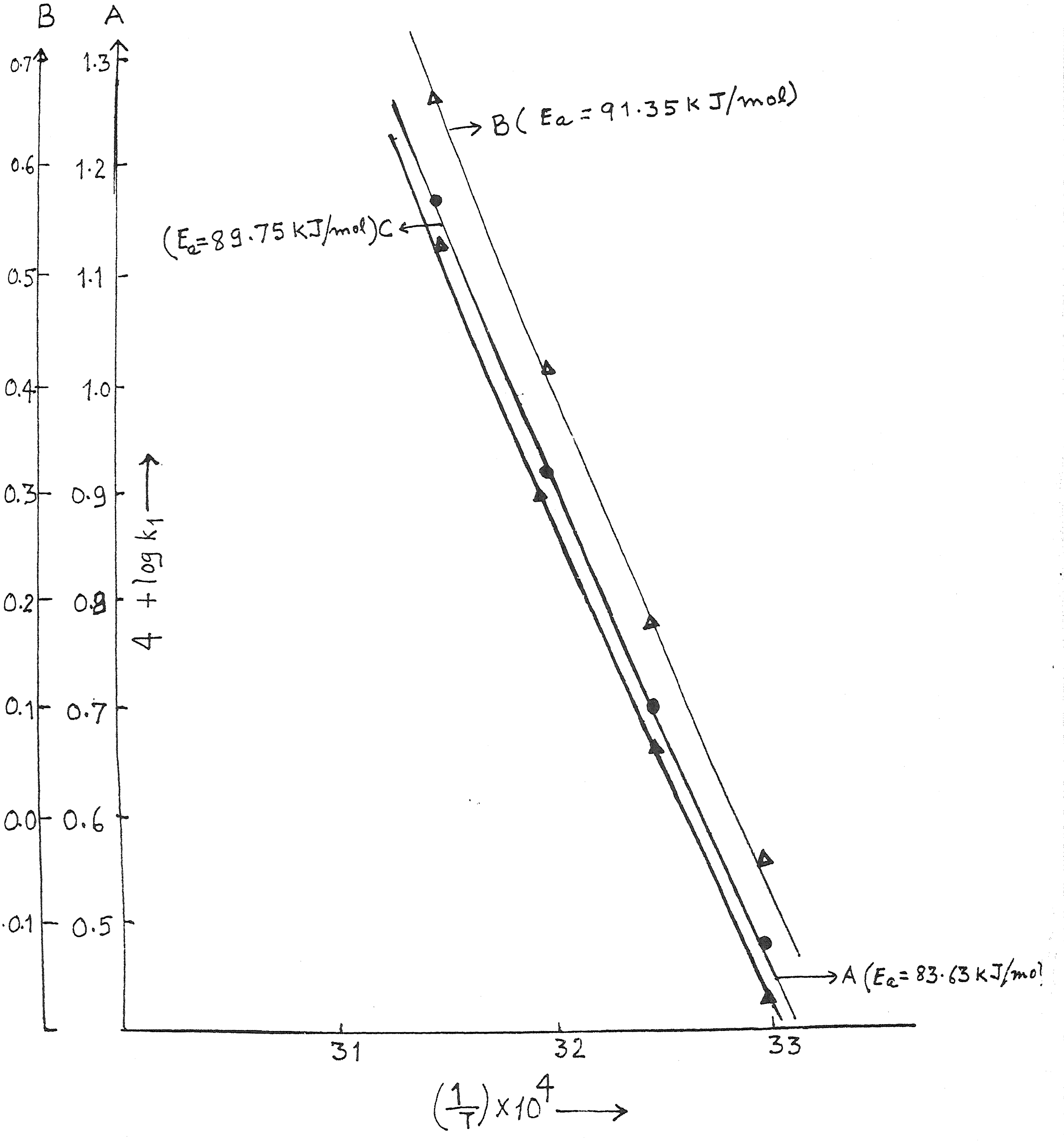

FIG. 11.1 : A → In OXIDATION OF GLYCINE
B → In OXIDATION OF ALANINE
C → In OXIDATION OF VALINE

It is clear from the data of above tables that on increasing the temperature the value of first - order rate constant increases. Now when log k_1 values were plotted against $\frac{1}{T}$, a straight line (Fig. 11.1) with slope equal to $-Ea/2.303R$ is obtained. Thus from the slope of the curve it is possible to calculate the value of E_a i.e. energy of of activation for oxidation of amino acids used here. The value of energy of activation for Ir(III) catalysed oxidation of glycine, alanine and valine by acidic solutions of N-bromosuccinimide are 84.63 kJ/mole, 91.35 kJ/mole and 89.75 kJ/mole respectively.

CHAPTER XII

INTERPRETATION OF RESULTS AND DISCUSSION

12 : This chapter deals with interpretation and discussion of experimentally obtained results and on the basis of such interpretations, an attempt would be made to propose the reaction scheme for Ir(III) chloride catalysed oxidation of amino acids viz. glycine, alanine and valine by acidic solutions N-bromosuccinimide in the presence of mercuric acetate as bromide ions scavenger. The reaction mechanisms for any reaction may be proposed on the basis of kinetic observations by many ways but only that mechanism is supposed to be correct which is capable of giving rate equation in complete agreement with observed kinetic facts. Before the reaction scheme for the reactions under investigation here is suggested, it is essential and worthwhile to discuss and ascertain the reactive species of various reactants involved in the reactions. Hence in order to ascertain the reactive species of N-bromosuccinimide, reducing amino acids and iridium (III) chloride in hydrochloric acid media, a careful observations of kinetic features are required. Therefore in the next sections kinetic results in summarised form and discussion on the reactive species of aforesaid reactants are described and thereafter final mechanism has been suggested in section 12.5.

12.1 : SUMMARY OF KINETIC OBSERVATIONS IN Ir(III) CATALYSED NBS OXIDATION OF AMINO ACIDS IN HYDROCHLORIC ACID

Following are key kinetic observations made in the title reactions.

(i) The reactions show first - order dependence on NBS at its low concentration range while first - order shifts to zero - order at higher concentration range.

(ii) All the reactions follow first - order kinetics with respect to each amino acid used here i.e. with respect to each of glycine, alanine and valine.

(iii) First - order dependence of the reactions on iridium trichloride was observed.

(iv) Variation of hydrochloric acid shows decreasing effect of hydrogen ions on the rate of oxidation of amino acids.

(v) Addition of succinimide in the reaction mixture of all reactions decreased the rate of oxidation of amino acids.

(vi) Addition of mercuric acetate did not bring about any change in the rate of oxidation of amino acids.

(vii) Addition of potassium chloride was found to have no significant effect on the rate of oxidation of amino acids.

(viii) Variation of ionic strength of the medium showed zero effect on the rate of oxidation of amino acids.

(ix) Temperature variation showed marked effect on the rate of NBS - Amino acids redox systems.

(xii) Corresponding aldehydes have been found to be reaction products.

12.2 : ASCERTAINING OF REACTIVE SPECIES OF N-BROMO-SUCCINIMIDE IN HYDROCHLORIC ACID

N-bromosuccinimide (NBS) has been already reported to exist in the following equilibrium.

$$NBS + H_2O \rightleftharpoons NSH + HOBr \quad \ldots \quad (1)$$

(Succinimide)

In acidic media NBS[1,2] may exist as given below :

$$NBS + H^+ \rightleftharpoons \overset{+}{NBSH} \quad \ldots \quad (2)$$

$$\overset{+}{NBSH} + H_2O \rightleftharpoons NSH + H_2OBr^+ \quad \ldots \quad (3)$$

or

$$NBS + H_2O \rightleftharpoons NSH + HOBr \quad \ldots \quad (4)$$

$$HOBr + H^+ \rightleftharpoons H_2O\overset{+}{Br} \quad \ldots \quad (5)$$

Thus from above equilibria it is clear that in acidic media oxidising species of NBS may be either NBS or $\overset{+}{NBSH}$ or HOBr or $H_2O\overset{+}{Br}$ (formed from set of equilibria

2 and 3 or from set of equilibria 4 & 5). Since reaction shows retarding effect of H^+ on the rate, therefore possibility of $NBSH^+$ and $H_2O\ Br^+$ is ruled out although negative effect of succinimide (NSH) is explained on assuming $H_2O\ Br^+$ as oxidising species. When NBS as such is taken as reactive species then succinimide effect should be zero contrary to observed its decreasing effect. This suggests that NBS can not be oxidising species as it will fail to explain the kinetic behaviour of reactions with respect to succinimide. Hence the only choice is $HOBr$ which can be taken as reactive species.

12.3 : REACTIVE SPECIES OF AMINO ACIDS IN HYDROCHLORIC ACID

Amino acids have been reported to exist as dipolar ionic form[3] in water. It exists as

$$R\overset{+}{N}H_3CO\overset{-}{O}.$$

In acidic media, amino acid might exist as $RCH_2(\overset{+}{N}H_3)COOH$ according to the following equilibrium

$$RCH_2\overset{+}{N}H_3CO\overset{-}{O} + H^+ \rightleftharpoons RCH_2\overset{+}{N}H_3COOH \qquad ...(1)$$

Thus in acidic media either dipolar ionic form or protonated amino acid may be reactive reducing substance. But if $RCH_2\overset{+}{N}H_3COOH$ i.e. protonated amino acid is taken as reactive species, it would require first - order dependence on H^+ contrary to our observed decreasing effect of H^+ on rate of reaction. This rules out the possibility of protonated species of amino acid as reactive species. Hence dipolar ionic form i.e. neutral amino acid (i.e. RCH_2NH_2COOH) is reactive species. This when assumed as reactive species gives rate low capable of explaining all observed kinetic data.

12.4 : REACTIVE SPECIES OF IRIDIUM (III) CHLORIDE IN HYDROCHLORIC ACID

In acidic medium iridium (III) chloride[4] has been reported to exist as given below :

$$IrCl_3 + 3\,HCl \rightleftharpoons IrCl_6^{3-} + 3H^+ \quad \ldots (1)$$

Further $IrCl_6^{3-}$ is also in equilibrium with $IrCl_5H_2O^{2-}$ according to the following equilibrium

$$IrCl_6^{3-} + H_2O \rightleftharpoons IrCl_5H_2O^{2-} + Cl^- \quad \ldots (2)$$

Thus there are three possibilities of reactive species in hydrochloric acid for iridium (III) chloride. These are $IrCl_3$, $IrCl_6^{3-}$ and $IrCl_5H_2O^{2-}$. Out of these $IrCl_6^{3-}$ and $IrCl_5H_2O^{2-}$ are ruled out as both of them require dependence of rate on chloride ions contrary to our insignificant effect on the rate of reaction. Hence the only choice left is neutral species $IrCl_3$. Hence $IrCl_3$ as such has been assumed to be real catalytic species.

12.5 : MECHANISM OF I_r(III) CATALYSED OXIDATION OF AMINO ACIDS BY N-BROMOACETAMIDE IN HYDROCHLORIC ACID

It has been concluded from the previous sections that $HOBr$ and neutral amino acid are oxidising species and reducing species of N-bromosuccinimide and amino acids respectively in acidic media. Since there is no significant effect of variation of chloride ions on the rate of the reaction hence I_rCl_3 as such has been taken as reactive species of the catalyst. For the sake of convenience, I_rCl_3 has been written as I_r(III) throughout mechanistic derivation.

Now considering the above statement and keeping the kinetic results into consideration, the following mechanistic steps are suggested. Here NBS, RCH (NH_2) COOH and NSH stand for N-bromosuccinimide, amino acid and succinimide respectively.

$$NBS + H_2O \overset{K_1}{\rightleftharpoons} NSH + HOBr \quad \text{... (i)}$$

$$I_r(III) + HOBr \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} I_r(III) - OBr^{2+} + H^+ \quad \text{.. (ii)}$$

$$I_r(III) - OBr^{2+} + RCH(NH_2)COOH \xrightarrow[\text{slow and rate determining step}]{} RCHO$$

$$+ I_r(III) + NH_3 + CO_2 + Br^- \quad \text{... (iii)}$$

where R stands for $-H$, $-CH_3$, $-CH(CH_3)$ in glycine, alanine and valine respectively.

The rate of the aforesaid reaction may be expressed in terms of rate of loss of concentration of succinimide i.e. $-d\,NBS/dt$.

Hence on the basis of above steps rate of the reaction may be written as

$$\frac{-d\ NBS}{dt} = \text{rate} = kd\ X\ AA \qquad \ldots (1)$$

On applying steady state approximation to the concentration of X we get eqn (2) with the help of steps (ii) and (iii)

$$\frac{d\ X}{dt} = 0 = k_2\ I_r(III)\ HOBr - k_{-2}\ X\ H^+ - kd\ X\ AA$$

$$\text{or } k_{-2}\ X\ H^+ + k_d\ X\ AA = k_2\ I_r(III)\ HOBr$$

$$\text{or } X\ \left(k_{-2}\ H^+ + kd\ AA\right) = k_2\ I_r(III)\ HOBr$$

$$\text{or } X = \frac{k_2\ I_r(III)\ HOBr}{k_{-2}\ H^+ + kd\ AA} \qquad \ldots (2)$$

On substituting the value of X from eqn (2) in eqn (1) we have eqn (3)

$$\frac{-d\ NBS}{dt} = \frac{k_d\ k_2\ Ir(III)\ HOBr\ AA}{k_{-2}\ H^{+} + k_d\ AA} \quad \ldots \quad (3)$$

Now the total concentration of $IrCl_3$ i.e. Ir(III) may be written as eqn (4)

$$Ir(III)_T = Ir(III) + X \quad \ldots \quad (4)$$

Now by comparing eqns (2) and (4) we have

$$Ir(III)_T = Ir(III) + \frac{k_2\ Ir(III)\ HOBr}{k_{-2}\ H^{+} + k_d\ AA} \quad \ldots \quad (5)$$

$$\text{or} \quad Ir(III)_T = Ir(III) \quad 1 + \frac{k_2\ HOBr}{k_{-2}\ H^{+} + k_d\ AA}$$

$$\text{or} \quad Ir(III)_T = Ir(III) \quad \frac{k_{-2}\ H^{+} + k_d\ AA + k_2\ HOBr}{k_{-2}\ H^{+} + k_d\ AA}$$

$$\text{or} \quad Ir(III) = \frac{Ir(III) \quad k_{-2}\ H^{+} + k_d\ AA}{k_{-2}\ H^{+} + k_d\ AA + k_2\ HOBr} \quad \ldots \quad (6)$$

On comparing eqns (3) and (6) we have

$$\frac{-d\ NBS}{dt} = \frac{k_d\ k_2\ HOBr\ AA\ Ir(III)_T\ \ k_{-2}\ H^+ + kd\ AA}{k_{-2}\ H^+ + k_d\ AA\ \ k_{-2}\ H^+ + k_d\ AA + k_2\ HOBr}$$

$$\text{or}\ \frac{-d\ NBS}{dt} = \frac{k_d\ k_2\ HOBr\ AA\ Ir(III)_T}{k_{-2}\ H^+ + k_2\ HOBr + kd\ AA} \qquad \ldots (7)$$

Since kd i.e. velocity constant for the slowest step is small hence $kd\ AA \quad < (k_{-2}\ H^+ + k_2\ HOBr$

Thus considering the above inequality eqn (7) becomes eqn (8)

$$\frac{-d\ NBS}{dt} = \frac{k_d\ k_2\ HOBr\ AA\ Ir(III)_T}{k_{-2}\ H^+ + k_2\ HOBr} \qquad \ldots (8)$$

Considering step (1) we have

$$K_1 = \frac{NSH\ HOBr}{NBS\ H_2O}$$

or $HOBr = K_1\ H_2O\ NBS\ /\ NSH$

$$\text{or}\ HOBr = \frac{K_1'\ NBS}{NSH} \qquad \ldots (9)$$

where $K_1' = K_1\ H_2O$

On substituting the value of $HOBr$ from eqn (9) in eqn (8) we have eqn (10)

$$-\frac{d\,NBS}{dt} = \frac{K_1' \, k_3 \, k_2 \; AA \; Ir(III)_T \; NBS}{NSH\left(k_{-2}\, H^+ + \dfrac{k_2\, K_1'\, NBS}{NSH}\right)}$$

$$\text{or} \quad -\frac{d\,NBS}{dt} = \frac{k_3 \, k_2 \, K_1' \; AA \; Ir(III)_T \; NBS}{NSH\left(\dfrac{k_{-2}\, H^+ \, NSH + k_2\, K_1'\, NBS}{NSH}\right)}$$

$$\text{or} \quad -\frac{d\,NBS}{dt} = \frac{k_3 \, k_2 \, K_1' \; AA \; Ir(III)_T \; NBS \; NSH}{NSH\left(k_{-2}\, H^+ \, NSH + k_2\, K_1'\, NBS\right)}$$

$$\text{or} \quad -\frac{d\,NBS}{dt} = \frac{k \; AA \; Ir(III)_T \; NBS}{k_{-2}\, H^+ \, NSH + k_2\, K_1'\, NBS} \qquad \ldots (10)$$

where $k = k_3 \, k_2 \, K_1$

It is evident from the rate law (10) that

(1) Order with respect to NBS at its low concentration is one when k_{-2} H^{+} NSH $\quad$ $k_2 K_1^{'}$ NBS and equation (10) becomes eqn (11)

$$\frac{-d\,NBS}{dt} = \frac{k\;AA\;Ir(III)_T\;NBS}{k_{-2}\;H^{+}\;NSH} \qquad \dots (11)$$

Again at higher concentration of NBS the I order tends to zero - order i.e. when $k_2 K_1^{'}$ NBS $\quad$ k_{-2} (H^{+}) NSH and eqn (10) becomes eqn (12)

$$\frac{-d\,NBS}{dt} = \frac{k}{k_2\,K_1^{'}}\;AA\;Ir(III)_T \qquad \dots (12)$$

The rate eqn (10) clearly shows first order in both $Ir(III)$ and amino acid i.e. AA. It also explains decreasing effect of H^{+} i.e. HCl and NSH.

It is also obvious from eqn (10) that Hg (II) is no involved in the reaction except its role as scavenger for

for bromide ions. It also explains zero effect of chloride ions i.e. KCl addition.

Since the rate law (10) has been derived on the basis of mechanistic steps (i - iii)) which involve interaction between a cation and a neutral molecule in the slow and rate determining step. Such interaction requires zero effect of ionic strength of the medium which has been experimentally also observed. Hence rate law (10) also explains negligible effect of ionic strength of the medium on the rate of oxidation of the amino acids. Hence the proposed mechanism seems to be valid.

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